



For Reference

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THE REACTIONS OF WATER GAS MIXTURE
OVER CATALYSTS AT HIGH PRESSURE AND THE PRELIMINARY
EXPERIMENTS ON THE SOLUBILITY OF METHANE IN HEXANE
UNDER PRESSURE

-by-

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University of Alberta, 1932.

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THIS IS

1. The reaction in mixtures of hydrogen and the oxides of carbon at high pressures and elevated temperatures over catalysts.

-and-

2. Preliminary experiments on the solubility of methane in hexane at pressures to 250 atmospheres.

Submitted in partial fulfilment of the
requirement for the degree of Master of
Science.

by

GEORGE H. ARGUE.

Under the direction of

Dr. E. H. BOOMER.

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GENERAL

INTRODUCTION

The researches to be reported in what follows comprise part of a more comprehensive investigation on the utilization of natural gas. As is well known, Alberta possesses extremely large supplies of natural gas, particularly in the area known as the Turner Valley field. No precise estimate of the reserves of gas available has been possible, but from a potential open flow of more than 600,000,000 cu. ft. per day, after several years operations under a driving pressure of 1000 to 1500 lbs. per sq. in., it is obvious that these reserves must be enormous.

It is well known that mixtures of carbon monoxide and hydrogen or carbon dioxide and hydrogen can be prepared readily by the controlled partial oxidation of the gaseous saturated hydrocarbons making up these natural gases.

These mixtures of hydrogen and the oxides of carbon are of great interest in view of the syntheses possible over catalysts at high pressure and temperature. The well known modern development of methanol synthesis may be mentioned as a successful application. The first part of the present research deals with an investigation of the reactions of these gas mixtures over a wide variety of mixed catalysts.

The literature includes a great deal of such work at ordinary pressures but has only in recent years given evidence of much work on catalyst mixtures at high pressures.

The present work was carried out from the point of view of determining the relations, if any, between the catalyst composition and the resulting reaction; the mechanism of the reaction occurring; and lastly, to determine the possibility of preparing higher alcohols than methanol, with particular reference to ethanol.

The second part of this report covers the preliminary work on an investigation of the liquid-vapor equilibrium in poly-component hydrocarbon systems. From the practical point of view this type of work is very necessary for the complete understanding of the conditions in such industrial equipment as the modern cracking still or the hydrogenation autoclave. The relation of natural gas to casing head gasoline, naptha and petroleum can only be completely understood when such data, as are to be described, become available. It is not impossible that, given the equilibrium conditions of such mixtures as appear at the separators under high pressure, the actual physical and chemical conditions in the producing sands could be stated.

From the theoretical point of view the equations for simple ideal systems have long been known but have lacked experimental confirmation in most instances. Most previously reported work has

been concerned with the composition of one phase alone, and has dealt with very unlike components. It is hoped in the present work dealing with simple saturated hydrocarbons that some degree of correlation may be found in as much as the systems used are at least approximately ideal. In any event an empirical expression relating the composition of each phase to the pressure and the temperature can be found.

PART 1

The reaction in mixtures of hydrogen and the oxides of carbon
at high pressures and elevated temperatures over catalysts.

April, 1932.

GEORGE H. ARGUE.

P A R T 1

INTRODUCTION

The reactions of mixtures of carbon monoxide and hydrogen have received a great deal of attention elsewhere. Investigations in all parts of the world have been carried out from the theoretical and practical standpoints. The possible reactions between the gases are comparatively few in number, but the secondary reactions among the primary products themselves and with the gases are very numerous. The nature of the products is extremely varied and depends very much on the conditions of pressure and temperature and the activity of the catalyst employed. Pure individuals or mixtures containing great numbers of individuals may be obtained.

The present work is a direct continuation of previous work along the same line and described in detail by Mr. H. E. Morris (31). The work to be reported covers only the reactions of CO₂ and H₂ and CO and H₂ mixtures over a wide variety of catalyst mixtures at pressures from 1000 to 3000 lbs. per sq. in. over the temperature range 200° C to 450° C. The primary practical object of determining the conditions necessary to ethanol formation has not been reached. That ethanol cannot be formed in appreciable amounts has been the conclusion of other investigators. The formation of ethanol undoubtedly would be a secondary step in the reaction, and it is very unlikely that the reaction could be controlled so as to stop at the proper point. In general, experience has shown that the

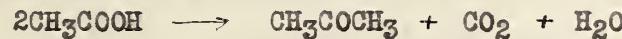
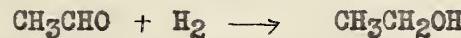
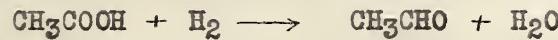
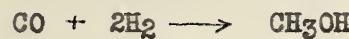
control of the product is nearly impossible once the reaction proceeds beyond the point of methanol formation.

On the theoretical side considerable uncertainty exists as yet with regard to even the simple primary reactions. The present work has in view the determination of the reaction mechanism of these primary steps. Before an understanding of the source of the multitudinous products is at all possible, the mechanism of these primary reactions on the catalyst surface must be determined.

LITERATURE REVIEW

Sabatier and Sendrens had realized the possibility of combining carbon monoxide and hydrogen to produce formaldehyde and methanol, but their experiments carried out at atmospheric pressure led to the formation of methane. In 1913 the Babische Anilin und Soda Fabrik secured promising results using supported catalysts of zinc, chromium, cobalt, manganese, molybdenum, or their oxides at elevated temperatures and pressures.

Fischer (1) used an iron catalyst impregnated with alkali and obtained a product containing aliphatic alcohols, ketones, aldehydes, acids and hydrocarbons which separated into two layers. The oily layer was called "Synthol" and was suitable as a motor fuel. A number of possible mechanisms of reaction were suggested to account for these products.



In 1924 Patart (2) circulated water gas over a zinc oxide catalyst at 400°C and 150 atmospheres pressure; a sample of pure methanol was collected. The oxides of chromium and vanadium were

also employed, and with the addition of copper to each one better results were obtained.

Audibert and Raineau (3) secured up to 95% conversion of the reacting carbon monoxide to methanol with mixed catalysts containing zinc, copper and other metals, prepared by co-precipitation as hydroxides from a solution of the nitrates. Manganese and chromium were active to a lesser degree.

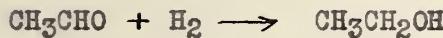
Lewis and Frolich (4) using a zinc-copper-aluminium catalyst, supported on copper to prevent overheating, obtained practically pure methanol. They gave the following mechanisms to account for the products of the reaction.



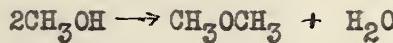
In a later paper, by the use of an iron alkali catalyst and an alkaline zinc chromium catalyst, they obtained a condensate which separated into two layers and contained propanol and a trace of ethyl alcohol, in addition to methanol.

Frolich, Fenske, Taylor and Southwich (5) investigated catalysts with varying proportions of zinc and copper and secured maximum yields of methanol with a mixture of 70 parts of zinc oxide and 30 parts of copper oxide. Morgan Taylor and Hedley (6) satisfactorily employed reactions over normal and basic zinc chromates at $350^{\circ} - 400^{\circ}\text{C}$ and 200 atmospheres in order to obtain

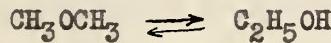
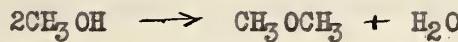
methanol. With catalysts containing alkalies and also with methanol catalysts to which cobalt was added, they secured small yields of higher alcohols. They suggested a mechanism of reaction with formaldehyde intermediate to account for the presence of these alcohols.



Later Brown and Galloway (7) isolated dimethyl ether along with methanol from a zinc-chromium catalyst. Evidently the dehydration of the alcohol occurred.



No trace of ethanol was found even though it was isomeric with dimethyl ether. Frolich and Fenske (8) were able to obtain a good yield of MeOH using a zinc-copper-chromium catalyst at 300°C. Frolich and Cryder (9) secured the maximum conversion of carbon monoxide to methanol with a zinc chromium catalyst, the constituents in the ratio of four to one, at 370° - 390°C. Later they suggested the following reactions to account for the formation of higher alcohols.



A mixture of the basic carbonates of zinc and manganese and potassium chromate gave higher alcohols by the slow condensation and dehydration of methanol. No dimethyl ether was isolated and an excess of carbon monoxide tended to appear as carbon dioxide in the exit gas, thereby removing water according to the reaction.



In 1930 Smith and Hirst (10), using mixtures of hydrogen and carbon dioxide under pressure with a catalyst containing four moles of zinc oxide to one mole of chromic oxide at 300°C, found evidence for the following reactions,



Mussbaum and Frolich (11) noticed that the maintenance of a high temperature during reduction caused a loss of activity in the catalyst. From large amounts of synthetic methanol Graves (12) was able to isolate normal propanol, isobutanol and a trace of ethanol by fractional distillation. 48% of the crude products were primary alcohols. The condensation of methanol was suggested as the most likely mechanism for the synthesis of these higher alcohols.

Plotnikov, Ivanov and Pospekhov (13) obtained methanol, water and a trace of ethanol from a zinc-chromium catalyst. With zinc-copper, chromium-copper and zinc-chromium-copper catalysts they

secured good yields of methanol from water gas mixtures. Methane water and carbon dioxide were also formed. The addition of alkali was found to decrease the catalytic activity.

Natta and Casazza (14) suggested that the preferential adsorption of hydrogen from water gas mixtures by a catalyst would point to a large yield of methane during subsequent reactions; while those catalysts which favored the adsorption of carbon monoxide tended to produce large amounts of methanol. Taylor and Kistiakowsky (15) estimated that mixtures of the oxides of zinc and chromium were more efficient than zinc oxide due to their increased adsorption of hydrogen, carbon monoxide and carbon dioxide. This was known to be true experimentally.

Wetburg and Dodge (16) have attempted to calculate the equilibrium constants and free energy changes in the formation of methanol from hydrogen and carbon monoxide. Smith, (18) Galloway, (19) Morgan, (6) and later Dodge (17) endeavored to check the experimental values of the equilibrium constants with theory and failed. As yet no exact information on the true equilibrium is available. The experimental calculations of equilibrium quantities cannot be relied on, due to the side reactions that occur even during the time the reactants are in contact with the catalysts. Theoretically, the calculation depends on the measurement of small differences between large thermal quantities; where a small relative error in the thermal

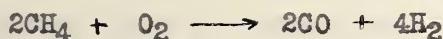
data results in a large relative error in the free energy and equilibrium constants.

EXPERIMENTAL

Materials and Storage

Two gas mixtures were used in this work. Electrolytic hydrogen and commercial carbon dioxide were taken from cylinders and allowed to mix in a gas holder in the ratio of two to one. The gas was dried by passing through CaCl_2 , compressed and sent to storage. The water gas mixture was prepared by the partial oxidation of methane at 1000°C over a nickel catalyst supported on asbestos. Viking natural gas of the approximate composition, CH_4 93%, C_2H_6 3%, N_2 4%, was mixed with oxygen in the ratio of two to one.

The reaction



took place and the water gas had an average composition of H_2 63.5%, CO 30%, N_2 5%, with small amounts of CO_2 and CH_4 . The gas was collected in a large holder, dried, compressed and sent to storage.

When desired oil vapours were removed by passing the compressed gas over scrap sheet metal contained in a long oil trap. Further purification by removal of water and in the case of water gas only, of CO_2 , was possible by sending the compressed gas through purifiers containing CaCl_2 and KOH .

The storage system consisted of four units which were utilized for methane, hydrogen, water gas and the hydrogen-carbon dioxide mixture. Each storage consisted of two cylinders, one of carbon steel with a capacity of 15 litres, the other a 5 litre chrome vanadium steel cylinder. By means of single, double and four way valves, the gas from the compressor could be purified as desired or

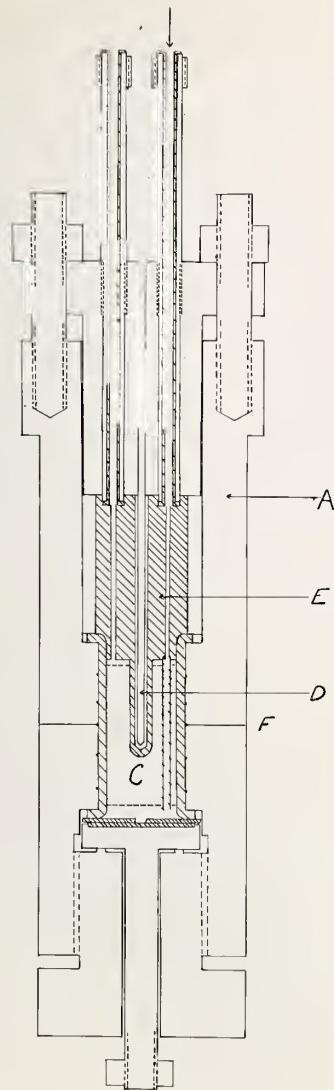
sent directly to any one of the storage systems. The exit from each storage was fitted to a four way valve so that any of the four gases were readily available in the experimental apparatus. Chrome molybdenum steel tubing $1/4$ " by $1/16$ " was used with four way plugs and connections of carbon steel. The necessary protective devices in the form of relief valves were placed on each stage and the delivery side of the compressor. Pressures on the storage system were indicated by standard hydraulic gauges behind protective screens.

Before entering the reactor, the pressure was measured on a calibrated recording pressure gauge. The gas was further purified by passing through activated charcoal in an all bronze purifier. The final purification was designed to remove any iron carbonyls present and to prevent the deposition of iron on the catalyst. Beyond this point the gas did not come in contact with any iron or ferrous alloy; all inside surfaces being copper or non ferrous material.

Reactors

The first autoclave used in this work, shown in Figure 1, was made of an austenitic alloy steel. Inlet and outlet tubes of copper lined tool steel extended through the top closure to the copper lined reaction chamber C. At no point did the gas come in contact with the steel, since the entire enclosed space was lined with copper, which is represented by cross hatching in the diagram. The copper block E, confined in a steel ring, formed the seal at the

FIGURE (1)



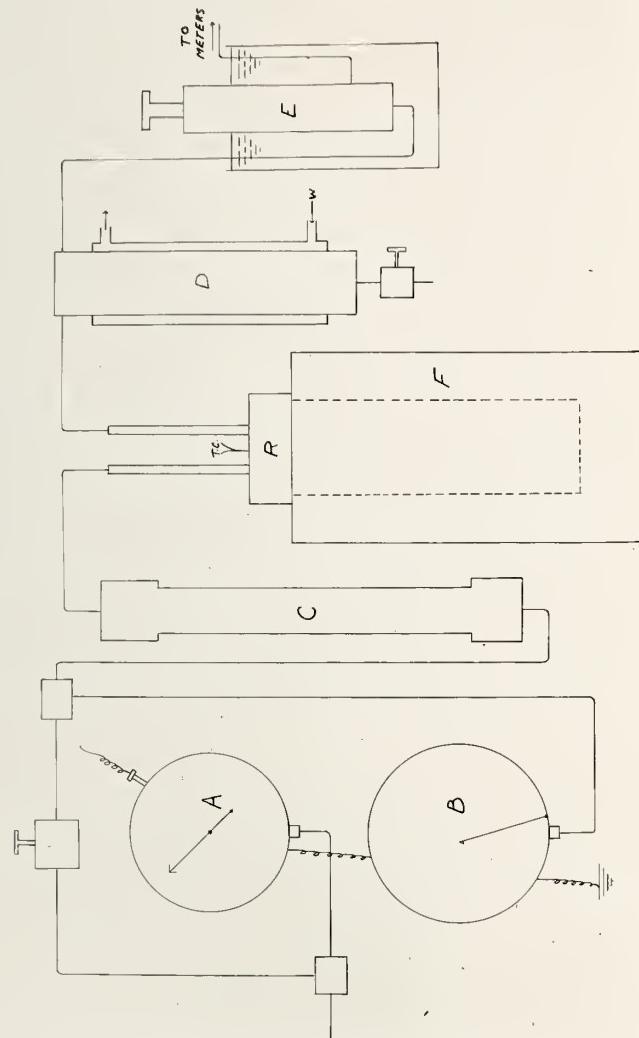
top of the reaction chamber; while a thin copper gasket on the face of the lower plug formed a gas tight joint. The copper thermocouple well, integral with the block E was reinforced by an inner steel lining and extended to the centre of the catalyst chamber. Spaced around the outer reactor wall were 1/32" holes which terminated in 1/32" grooves cut in the inner steel surface, thus allowing the escape of gas driven out of the steel and eliminating any danger of buckling the copper lining. The gas passed down the inlet tube, through the lower distributing plate into the space around the catalyst. At the outlet there was a similar plate packed with asbestos fibre to prevent the loss of catalyst on sudden surges of the gas.

The second reactor was of austenitic nickel chromium steel with end plugs of bronze held by steel nuts. It was 10" long with an internal diameter of 7/16" and was copper lined. The catalyst was held in place by copper screens and asbestos plugs. The flow was from end to end. A split brass sleeve provided uniform temperature distribution while a groove cut on the inside of the sleeve carried the thermocouple.

In both cases the autoclaves were heated by split multiple unit electric furnaces. Iron constantan thermocouples were used, and the temperature was measured and controlled by a two point Leeds and Northrup potentiometric recorder controller. The temperature was constant to within 5°C at all times.

The products of the reaction passed to a high pressure bronze

FIGURE (2)



condenser of approximately 65 c.c. capacity, which was surrounded by a copper water cooler. The liquids could be blown off through a valve connected to the bottom of the condenser. The gases were released to atmospheric pressure in a valve of duraluminum body with a bronze stem. The valve was surrounded by an oil bath which was kept above 110° C. After passing through ice-cooled condensers and a capillary flow meter the gas was sampled and then measured in a wet test meter filled with mineral seal oil.

The arrangement of the apparatus may be seen in the line diagram Figure 2. B is the recording pressure gauge. C. is the purifier filled with activated charcoal. Leading to the autoclave R in the electric furnace F, are shown the thermocouple leads T.C. D is a high pressure bronze condenser which leads to the expansion valve E in the oil bath. A copper lined draw-off valve is shown attached to the high pressure condenser D. The diagram also shows a standard indicating gauge A, fitted with contacts for operating a pressure regulator. This regulator was not in general used.

Analytical Measurements

The liquid products were blown out of the high pressure condenser into an ice-cooled condenser at atmospheric pressure. Qualitative tests were made for the presence of EtOH, aldehydes, and acids; then the liquid was fractionated in a micro column similar to that described by Cooper and Fasce (20) and the identification of the constituents was made by their boiling point. In some cases precipitates formed in the liquid when the

T A B L E 1

<u>No.</u>	<u>Constituents</u>	<u>Mole ratio of metals</u>
104	ZnO Cu Al ₂ O ₃	1: 1; 1
118	ZnO Cu Al ₂ O ₃	3: 2: 2
117	ZnO Cu Al ₂ O ₃	2: 1: 1
105	Cupric Phosphate	-
106	Ferric Phosphate	-
107	Nickelous Phosphate	-
111	Ferric Borate	-
113	Cupric Silicate	-
137	Cupric Silicate (a)	-
136	Chromic Silicate (a)	-
143	Zinc Chromic Silicate (a)	-
144	Zinc Cupric Silicate (a)	-
115	ZnO Co Al ₂ O ₃	4: 1: 1
116	ZnO Co Al ₂ O ₃	1: 1: 1
8	Iron, granulated	-
135	Ni CO ₃	-
132	Co ZnO MnO ₂ + 10% Fuller's earth(b)	2: 1: 2
133	Cu MnO ₂ Co by ignition (b)	1: 1: 0.01
134	Co MnO ₂ ZnO by ignition (b)	1: 0.7: 0.35
141	Basic ZnCrO ₄ (b)	-

T A B L E 1 (CONT'D)

<u>No.</u>	<u>Constituents</u>	<u>Mole ratio of metals</u>
122	Co Cu Al ₂ O ₃	1: 1: 1
121	Pb Cr ₂ O ₃ Mo	1: 1: 1
120	MgO Al ₂ O ₃ MnO ₂	1: 1: 1
127	ZnO Al ₂ O ₃ MnO ₂	1: 1: 1
119	ZnO Cu MnO ₂	1: 1: 1
128	ZnO Ag Pb	1: 1: 1
126	ZnO Fe Cr ₂ O ₃	1: 1: 1
124	ZnO Fe Cu	1: 1: 1
130	MgO Cu Al ₂ O ₃	1: 1: 1
129	CdO Cu SnO	1: 1: 1

(a) Holmes and Anderson . Ind. Eng. Chem. 17, 280, 1925.

(b) Morgan, Taylor and Hedley. J. Soc. Chem. Ind. 47, 117T, 1928.

pressure was released or when the liquid was boiled; these were tested qualitatively for the metals likely to be present.

The gases were analysed in a United States Steel Type of Bureau of Mines gas analysis apparatus. Carbon dioxide was measured by adsorption in 50% KOH; unsaturated hydrocarbons in fuming H₂SO₄ and oxygen in alkaline pyrogallol. H₂ and CO were oxidized over CuO at 300°C and measured by the decrease in volume and the formation of CO₂, respectively. CH₄ and C₂H₆ were calculated from the decrease in volume and the formation of CO₂ during the slow combustion with O₂ over a hot platinum wire.

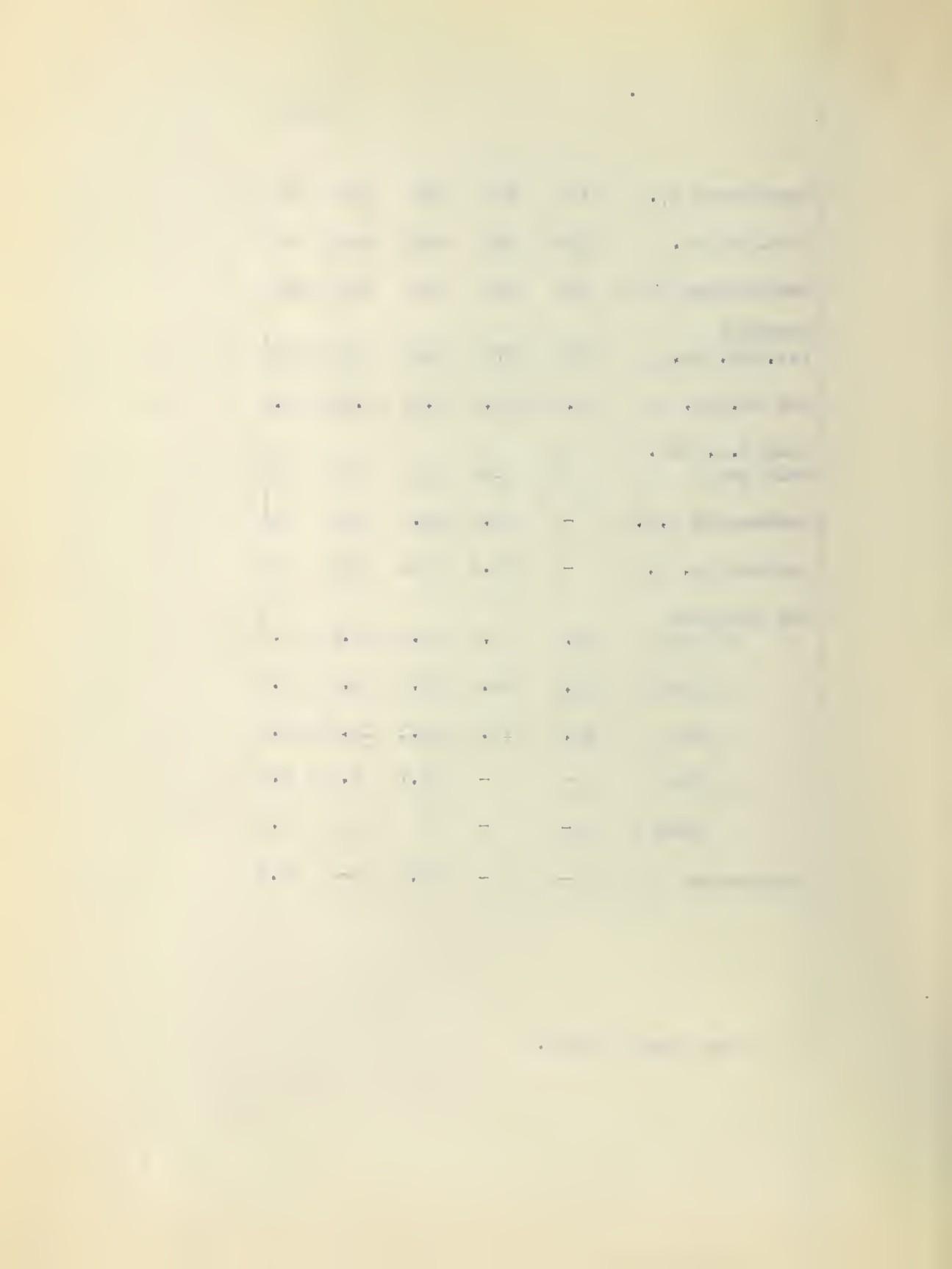
Catalysts and their preparation

The formula or composition of the catalysts examined in this work are given in Table 1. In all cases of the mixed oxide catalysts listed in the table, except where noted, the method of preparation was the same. The desired quantities of the metals as their nitrates were dissolved in water and 50% KOH added to neutrality. The precipitate was washed by decantation until free of all electrolyte, filtered, dried at 110°C, and crushed. The catalyst was placed in position in the reactor for reduction with hydrogen or water gas at 300°C. The procedure used in preparing the other catalysts was identical except in the initial formations which, where not obvious, are given by reference or otherwise.

T A B L E 2

Experiment No.	73	74	105	106	108	109	111	112	114	119	120	122	124	174	187	190	94	101	96
Catalyst No.	104"	104	104"	104	104	104	104	104	104	104	104	104	104	104"	104"	104	118"	118	118
Temperature °C	300	350	300	325	325	350	375	325	325	275	250	225	200	300	300	300	300	325	350
Pressure lbs./sq. in.	2500	2725	2175	2050	2050	2650	2400	1025	2275	1950	1800	1900	1700	2450	2325	2350	1700	1825	1425
Gas cu. ft.	8.22	6.8	2.67	3.83	2.2	2.78	1.83	2.15	3.53	4.86	4.85	7.1	3.14	2.85	2.2	2.33	9.7	6.37	4.98
Flow c.c./min. exit gas	160	145	65	85	100	115	80	110	160	110	150	145	140	75	160	120	105	120	125
Condensate c.c.	-	3.5	71.5	65	44	52	21.5	2	65	66.5	19.0	8.5	0	61	50	50	60	22.5	12
Methanol c. c.	-	0.5	71	64	42	50	20	0.5	61	60	18.5	8.0	0	61	50	50	59	20.0	10
Gas Analysis																			
CO ₂	1.0	3.5	3.4	13.9	7.4	10.0	14.3	25.7	-	4.3	3.4	2.9	2.0	1.5	5.1	-	2.7	3.8	4.3
H ₂	62.8	65.0	59.3	55.4	60.5	60.5	59.5	66.2	-	59.5	60.0	59.2	60.7	62.4	57.5	-	63.5	62.0	58.3
CO	25.6	16.5	28.1	16.4	18.4	16.2	12.2	4.3	-	26.7	28.9	21.9	29.3	25.2	16.4	-	21.8	21.4	23.3
CH ₄	-	-	3.7	3.9	4.4	2.6	3.4	3.7	-	0.9	0.7	-	2.3	4.3	4.6	-	2.6	2.9	4.8
C ₂ H ₆	-	-	0	0	0.5	0.8	2.5	0	-	0	0	-	0	0.2	0	-	0.4	0	0
Conversion	-	-	65.2	-	67.3	68.9	64.0	-	-	48.0	-	-	-	62.7	-	-	35.7	22.6	14.6

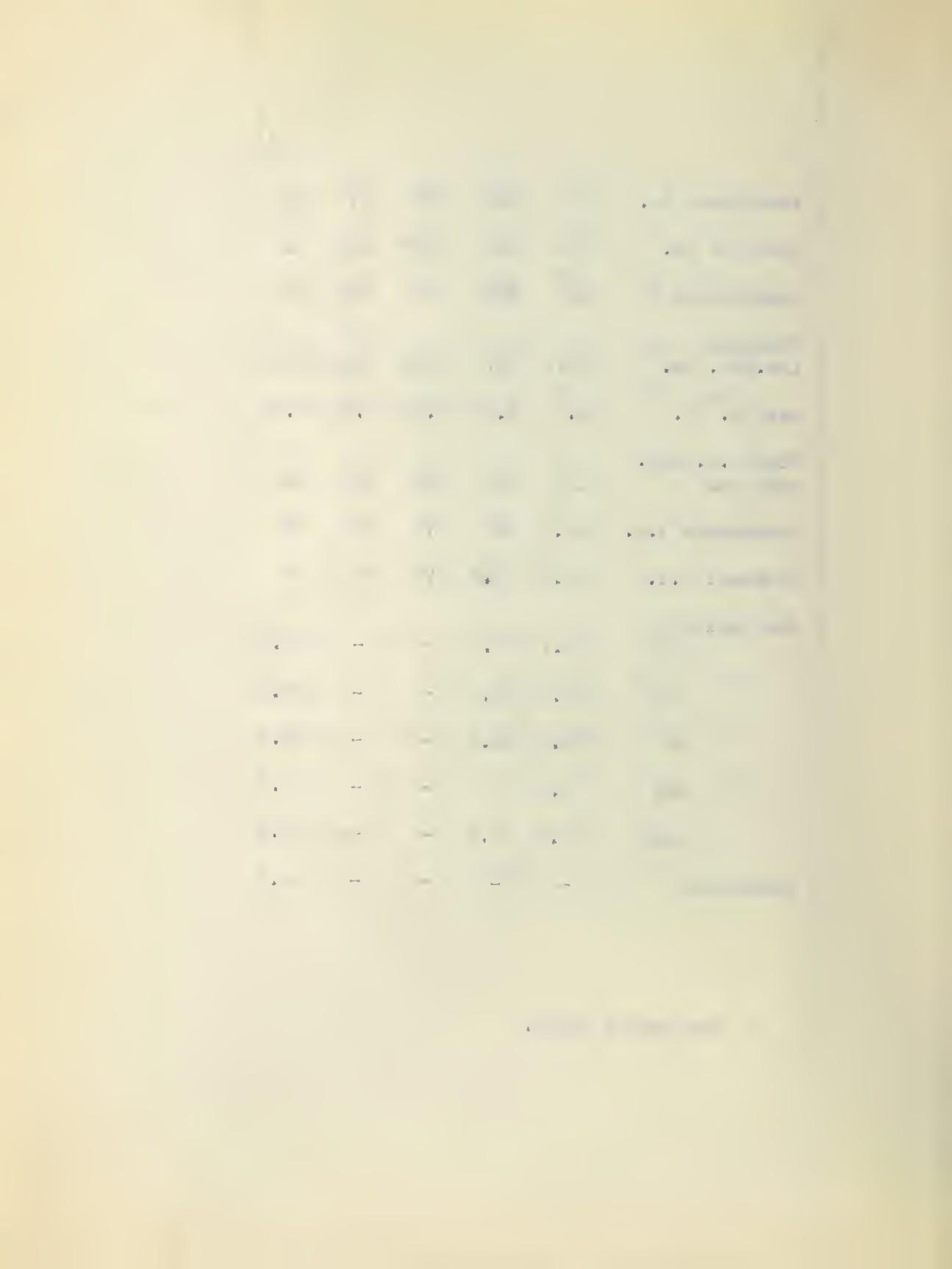
" New sample taken.



T A B L E 2 (CONT'D)

Experiment No.	98	103	178	179	180	86	87	88	90	91	110	113	115	117	118	184	80	81	121
Catalyst No.	118	118	118"	118	118	117"	117	117	117	117	117	117	117	117	117	117"	105"	105	106"
Temperature °C	400	300	300	300	300	300	350	400	400	350	300	300	375	450	250	300	300	450	300
Pressure lbs./sq. in.	1375	1375	2550	2500	2500	1375	1375	1375	1600	1375	2650	2275	2050	1950	1950	2225	1950	1825	1850
Gas cu. ft.	11.61	6.18	2.37	2.94	3.89	5.04	6.07	6.90	5.61	36.07	1.82	4.87	5.68	5.28	4.49	2.5	3.3	7.35	2.41
Flow c.c./min. exit gas	130	110	140	110	110	100	130	150	145	150	80	205	180	125	110	150	65	115	70
Condensate c.c.	15.5	12	37	50	67	16.5	14.5	19.5	26.1	51	12	36	10	3	2	25	0	0	0
Methanol c.c.	12.5	9.3	37	50	67	12.5	6	2.2	0	5.4	11.5	34	-	-	-	25	0	0	0
Gas Analysis																			
CO ₂	6.7	2.7	-	-	3.0	12.2	15.7	17.6	24.2	9.4	4.8	3.6	3.7	6.2	2.7	5.5	1.8	2.0	1.4
H ₂	57.5	61.3	-	-	60.2	57.7	52.0	48.1	45.4	55.6	60.5	60.4	65.5	59.3	60.8	55.6	60.3	61.8	61.4
CO	22.7	24.4	-	-	20.3	12.2	9.8	7.3	5.2	19.0	26.3	28.5	25.1	25.1	28.7	17.9	24.1	23.0	30.5
CH ₄	4.4	0	-	-	5.2	8.5	13.5	13.6	22.2	7.5	2.1	1.8	1.9	5.2	0.9	7.3	6.2	6.3	1.0
C ₂ H ₆	0.3	2.5	-	-	0.9	2.2	3.5	6.6	0	2.2	0.3	0	0.5	2.2	0	0	0	0	0
Conversion	-	-	-	-	62.7	28.9	-	-	-	-	32.4	32.7	-	-	-	52.6	-	-	-

" New sample taken.



T A B L E 2 (CONT'D)

Experiment No.	123	126	127	85	125	128	130	168	167	169	209	210	211	76	77	78	79	82	83
Catalyst No.	106	107"	107	111"	113"	113	113	137"	136"	136	143"	143	144"	115"	115	115	115	116"	116
Temperature °C	450	300	450	425	300	300	450	300	300	400	300	400	300	300	300	325	275	300	300
Pressure lbs./sq. in.	1700	2450	2200	2000	2200	2100	2050	2100	2100	2075	1225	1125	1025	2725	2425	2425	2150	2125	1825
Gas cu. ft.	4.1	3.63	4.49	8.86	1.2	2.2	4.3	3.17	1.69	2.3	3.53	3.33	4.75	18.17	6.99	5.88	7.01	7.17	5.25
Flow c.c./min. exit gas	180	150	180	190	-	-	140	115	65	110	240	150	150	240	140	130	160	140	100
Condensate c.c.	0.1	1	1	0	1	0.5	0	0.5	0	0.5	0.2	1.5	3	7	8.5	3	1	14.5	64
Methanol c.c.	0	0	0	0	0	0	0	0	0	0	0	0	0	2.9	0.5	0	-	0	0
Gas Analysis																			
CO ₂	1.5	1.2	2.0	-	-	-	1.1	1.6	1.6	1.9	2.8	7.0	1.1	-	29.1	7.0	3.4	5.7	-
H ₂	59.6	60.7	61.0	-	-	-	62.3	62.5	63.4	64.2	61.2	56.5	60.3	-	62.5	55.3	56.4	45.5	-
CO	29.9	30.7	30.3	-	-	-	30.6	28.5	24.6	25.3	25.6	20.5	27.9	-	1.5	22.1	26.3	22.7	-
CH ₄	3.2	-	2.2	-	-	-	0.2	2.7	0.8	0.4	2.6	8.3	4.4	-	4.1	10.2	5.4	18.9	-
C ₂ H ₆	0	-	0	-	-	-	0.8	0	1.5	1.9	0	0	0	-	0	0	0	0	-
Conversion	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

" New sample taken.

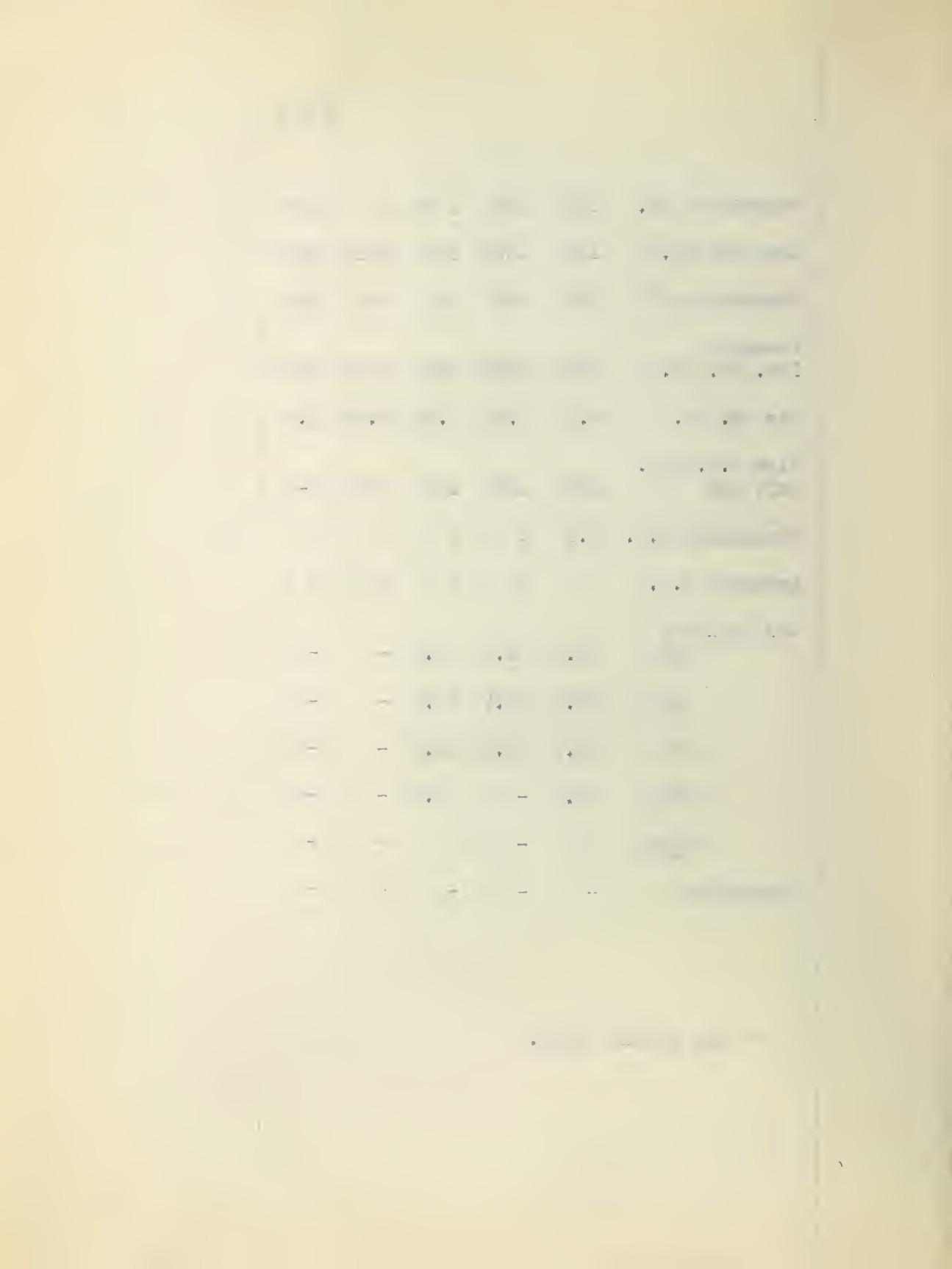


TABLE 2 (CONT'D)

Experiment No.	84	147	149	150	151	152	171	173	157	160	159	164	156	158	162	163	165	166	204
Catalyst No.	116	8"	8	8	8	8	135"	135	132"	132	132	132	133"	133	134	134	134	134	141"
Temperature °C	300	300	350	350	400	400	300	400	300	350	400	400	300	450	300	300	400	400	270
Pressure lbs./sq. in.	2175	1500	1150	1550	1825	2100	2575	2600	2750	2175	2450	1450	3175	2750	2900	2325	1450	1950	1775
Gas cu. ft.	12.0	9.46	4.66	3.94	6.69	3.29	1.83	6.52	3.41	5.51	3.98	5.9	0.22	2.88	2.62	3.07	4.31	3.32	3.4
Flow c.c./min. exit gas	240	120	110	110	260	155	65	140	135	140	135	125	-	115	85	165	95	220	460
Condensate c.c.	-	60	36	31	57	27	2.5	56	15	12.5	23	58	1	2	69	21.5	68	24	3
Methanol c.c.	0	1.4	0.5	0.1	0.4	0	0	0	0	0	0	0	-	0	0	0	0	0	0
Gas Analysis																			
CO ₂	22.1	19.6	20.2	30.2	31.3	19.3	2.4	19.1	18.5	20.3	20.4	-	0.7	4.3	36.3	30.3	-	21.9	2.7
H ₂	7.8	61.6	45.8	56.2	52.5	45.3	63.2	1.3	35.3	33.7	22.8	-	63.3	65.0	5.2	6.5	-	9.2	61.2
CO	3.2	3.8	8.0	5.4	5.2	0.6	22.6	1.2	6.4	4.5	2.9	-	28.4	20.4	0.9	1.3	-	1.2	24.3
CH ₄	48.4	3.5	8.9	4.2	5.8	14.7	0	73	29.5	30.7	44.2	-	1.4	5.0	51.2	52.2	-	51.9	0.8
C ₂ H ₆	-	5.1	7.6	2.3	3.9	9.0	3.4		1.1	0	0	-	0	0	2.5	2.5	-	2.7	1.6
Conversion	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

" New sample taken.

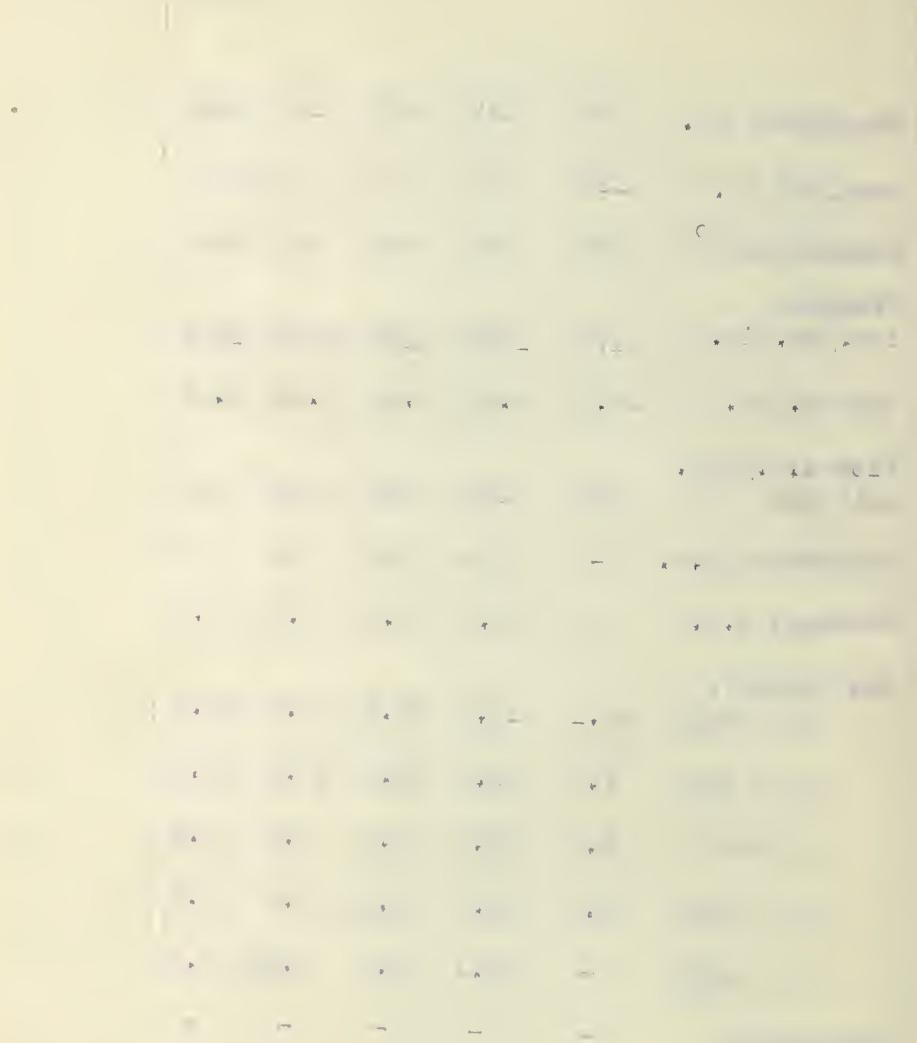
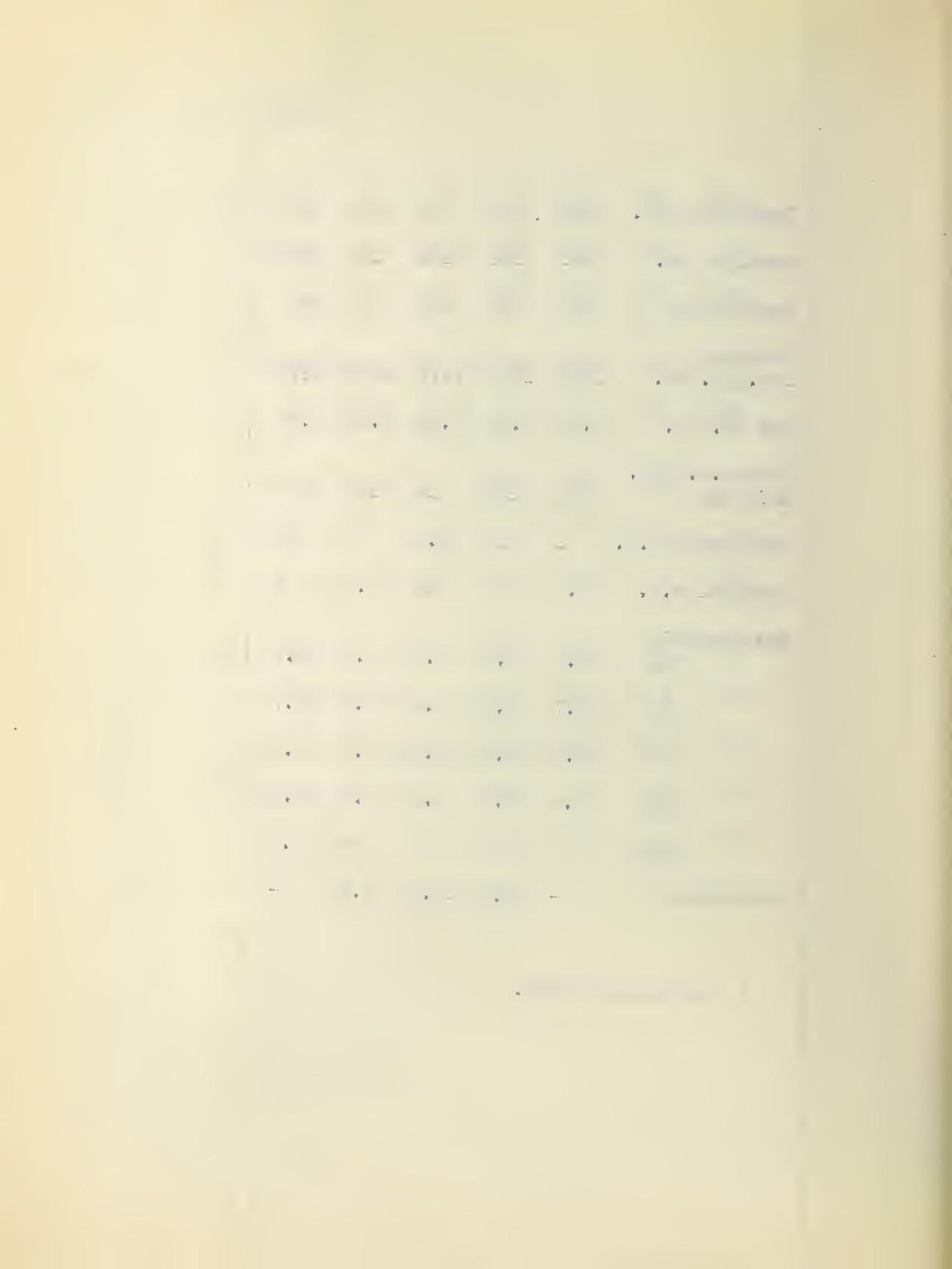


TABLE 2 (CONT'D)

Experiment No.	205	206	207	208	104	107	100	102	97	99	139	141	143	145	92	93	129	131	132
Catalyst No.	141	141	141	141	122"	122	121"	121	120"	120	127"	127	127	127	119"	119	128"	128	126"
Temperature °C	300	350	400	450	300	325	300	400	350	400	300	350	400	450	400	300	300	450	300
Pressure lbs./sq. in.	1650	1550	1475	1325	2175	2050	1825	1375	1425	1375	1975	1625	1425	1275	1500	1700	2050	2100	2450
Gas cu. ft.	2.35	5.63	4.64	4.44	6.83	3.11	5.14	4.98	4.71	5.10	4.25	1.72	3.24	2.72	7.0	9.71	3.55	3.52	3.29
Flow c.c./min. exit gas	170	150	110	120	105	75	90	115	95	95	80	90	110	120	-	105	140	120	135
Condensate c.c.	1	16	11.5	7	35	21	2	9.5	-	3.5	10	6.5	8	4	0	0	1	0	6
Methanol c.c.	0.5	16	11	4.5	0	0	1	0	-	2.5	8	6.5	5	2	0	0	0	0	1.0
Gas Analysis																			
CO ₂	3.2	3.8	5.6	5.6	22.7	21.2	13.1	17.5	3.3	4.0	4.2	6.0	5.9	7.6	-	2.3	1.9	1.7	3.2
H ₂	60.7	60.0	59.4	58.8	30.7	19.3	52.8	54.4	62.5	57.6	62.2	61.4	61.2	60.4	-	63.1	61.4	60.3	58.8
CO	24.2	25.4	23.4	23.6	3.2	2.3	13.0	-	24.7	25.2	27.1	25.1	25.0	23.7	-	24.2	28.3	30.5	16.9
CH ₄	3.8	3.7	2.9	3.6	29.3	42.4	13.0	16.8	3.8	3.2	1.1	1.3	1.6	1.2	-	2.0	0	2.6	2.6
C ₂ H ₆	0	0	0	0	3.8	1.3	2.1	0	0	2.1	0	0	0	1.3	-	0.5	2.7	0	1.9
Conversion	-	18.2	16.8	7.9	-	-	-	-	-	-	12.1	17.1	11.0	-	-	-	-	-	-

" New sample taken.



T A B L E 2 (CONT'D)

Experiment No.	135	136	137	134	138	140	142	144	146	153	154	170	172
Catalyst No.	126	126	126	126	124"	124	124	124	124	130"	130	129"	129
Temperature °C	350	400	400	450	300	350	400	450	300	300	450	300	400
Pressure lbs./sq. in.	2550	2500	2375	2450	1975	1625	1425	1275	1325	2100	2275	2575	2600
Gas cu. ft.	4.12	4.6	8.76	2.22	7.68	3.55	3.34	2.79	6.21	1.55	3.64	2.82	4.75
Flow c.c./min. exit gas	235	160	210	115	150	160	115	120	240	70	170	100	100
Condensate c.c.	2.5	8	13.5	3	35	20.5	19	12	12.5	8	3	0.5	1
Methanol c.c.	0	1.0	1.4	0	0.8	1.0	1.0	0	1.4	8	-	0	0
Gas Analysis													
CO ₂	5.5	8.5	-	11.4	16.7	19.4	19.0	18.6	11.8	-	8.2	0.5	1.5
H ₂	61.3	60.2	-	57.0	55.0	49.6	44.4	39.5	60.5	-	69.9	64.1	63.9
CO	25.6	21.7	-	17.5	11.9	8.0	9.6	8.3	13.7	-	7.8	27.6	25.6
CH ₄	0.7	2.4	-	5.2	3.2	10.2	9.9	13.6	6.5	-	9.3	1.7	1.8
C ₂ H ₆	1.4	1.5	-	2.9	5.3	4.1	4.5	7.6	0	-	-	0.9	1.1
Conversion	-	-	-	-	-	-	-	-	-	-	-	-	-

" New sample taken.

Experimental Results

The results are given in the single extended Table 2. The measurement of the volume of liquid products was approximate in some cases due to the loss of liquid on the sudden expansion from the high pressure condenser and also because of incomplete separation of constituents during fractional distillation. The volume of the incoming gas at high pressure could not be measured but in some cases it was calculated approximately from the total of the liquid products and the exit gas. The pressure as recorded was corrected and an average for the run was taken. In most cases the pressure drop during a run was 100 to 200 lbs. per sq. in. During an experiment the flow was controlled from observations of the flow meter on the exit gas, and served only as a rough measure of the rate of flow of gas over the catalyst.

The conversion to alcohol could be calculated from the weight of gaseous and liquid products. An example is here set down. In Experiment No. 174 with a zinc-copper-aluminium catalyst, 61 c.c. of MeOH were recovered along with 2.85 cu. ft. of gas. The compositions of the gases are given, in percentages.

	<u>Inlet Gas</u>	<u>Exit Gas</u>
CO ₂	1.3	1.5
H ₂	63.6	62.4
CO	26.2	25.2
CH ₄	3.6	4.3
C ₂ H ₆	-	0.2

The weight of any gaseous constituent will be given by the % by volume times the volume of the gas times a factor for the particular gas. The factor was the molecular weight of the gas times 28.32 times a correction to N. T. P. divided by 22.4.

Assuming the temperature is 25°C and the pressure 700 m.m.,

$$\text{the correction will be } \frac{700 \times 273}{760 \times 298} = 0.843$$

$$\text{The factor for CO}_2 = \frac{44 \times 28.32 \times 0.843}{22.4} = 46.8$$

$$\text{Similarly the factor for H}_2 = 2.14$$

$$\text{CO} = 29.8$$

$$\text{CH}_4 = 17.05$$

$$\text{C}_2\text{H}_6 = 32.0$$

The weights of the constituents in the exit gas were,

$$\text{CO}_2 \quad 0.015 \times 2.85 \times 46.8 = 2.01 \text{ g.}$$

$$\text{H}_2 \quad 0.624 \times 2.85 \times 2.14 = 3.81 \text{ g.}$$

$$\text{CO} \quad 0.252 \times 2.85 \times 29.8 = 21.5 \text{ g.}$$

$$\text{CH}_4 \quad 0.043 \times 2.85 \times 17.05 = 2.09 \text{ g.}$$

$$\text{C}_2\text{H}_6 \quad 0.002 \times 2.85 \times 32 = \underline{\underline{0.183 \text{ g.}}}$$

$$\text{Total weight of exit gas} = 29.593 \text{ g.}$$

$$\text{The weight of CH}_3\text{OH} = 61 \times 0.8 = 48.8 \text{ g.}$$

$$\text{Total weight of products} = 78.393 \text{ g.}$$

This value must also be the weight of the incoming gas.

It was necessary to calculate the average molecular weight of the inlet gas mixture in order to find its CO content as weight

percentage. The percent by volume of the constituents and the total weight were known. Obviously the sum of the products of the percent by volume and the molecular weight of each component in the gas gives the average molecular weight of the mixture. For the particular example chosen,

$$\text{CO}_2 \quad 0.013 \times 44 = 0.572 \text{ g.}$$

$$\text{H}_2 \quad 0.636 \times 2 = 1.272 \text{ g.}$$

$$\text{CO} \quad 0.262 \times 28 = 7.34 \text{ g.}$$

$$\text{CH}_4 \quad 0.036 \times 16 = \underline{\underline{0.574 \text{ g.}}}$$

$$\text{The average molecular weight} = 9.76 \text{ g.}$$

Then the percent by weight of CO in the inlet gas was

$$\frac{0.262 \times 28 \times 100}{9.76} = 75.2\%$$

$$\text{Weight of CO in the inlet gas} = 0.752 \times 76.393 = 58.9 \text{ g.}$$

$$\text{The weight of CO in the alcohol} = \frac{28 \times 48.8}{32} = 42.6 \text{ g.}$$

$$\text{Percent Conversion of CO to alcohol} = \frac{42.6 \times 100}{58.9} = 72.5\%$$

A rapid approximate method of calculating conversions based on volumes was as follows,

$$\text{The volume of CO in the exit gas} = 0.252 \times 2.85 = 0.718 \text{ cu. ft.}$$

The volume of CO in the alcohol will be the weight of alcohol times

a factor which is $\frac{22.4}{32 \times 28.32} = 0.0249$

$$\text{The volume of CO in MeOH} = 48.8 \times 0.0249 = 1.217 \text{ cu. ft.}$$

Therefore the total volume of gas as calculated from the products

$$= 1.217 + 0.718 = 1.935 \text{ cu. ft.}$$

$$\text{Conversion of CO to CH}_3\text{OH} = \frac{1.217 \times 100}{1.935} = 62.7\%$$

In this method no attention was given to the loss of CO in forming CO_2 , CH_4 or C_2H_6 or to the formation of CO from these molecules.

It has been assumed that all the CO has reacted according to the equation $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$.

It was known that this was not strictly true but errors in the sampling and measurement of the products and reactants were such, that the percent conversions calculated by this latter method were sufficiently accurate in most cases. In all examples which have been tabulated the approximate method has been used.

The space velocity is an important factor in industrial catalytic reactions. It is defined as the volume of gas per unit volume of catalyst passed per hour. The volume of CO which was converted to alcohol was calculated as before; two volumes of hydrogen were required per unit volume of CO. Then the total volume represented by liquid products was three times the volume of the CO in the alcohol. This was combined with the volume of exit gas and the space velocity calculated on the total volume. For example, in Experiment No. 174, 2.85 cu. ft. of exit gas were found. The quantity of CO converted to alcohol was the weight of the alcohol times a factor as given above.

$$\text{Volume of CO in the alcohol} = 48.8 \times 0.0249 = 1.217 \text{ cu. ft.}$$

$$\begin{aligned}\text{The total volume of gas represented by MeOH was} &= 3 \times 1.217 \\ &= 3.657 \text{ cu. ft.}\end{aligned}$$

$$\text{The total volume of gas} = 2.85 + 3.657 = 6.5 \text{ cu. ft.}$$

The volume of catalyst was 17 c.c. approximately and the reaction

was carried on for 6 hours.

$$\text{The space velocity} = \frac{6.5 \times 28.32 \times 1000}{6 \times 17} = 1800$$

The volume of the catalyst was difficult to measure since the volume decreased during reduction and shrinking and sintering frequently took place during the reaction. The space velocity is only approximate in most cases.

Experimental Results

The first catalyst, No. 104, which was investigated was an equimolar mixture of Zn, Cu and Al as oxides. In Experiments No. 105 and 174 conducted at 300°C the conversion of CO to CH_3OH was 65.2% and 62.7% respectively. The average space velocity was 1800. When the temperature was raised to 325°C the yield was 67.3% with a space velocity of 900. In one run, No. 112, using the H_2 and CO_2 mixture at a pressure of 1025 lbs. per sq. in., only a small amount of liquid was formed and the conversion was very small. This was not due to a loss of the activity of the catalyst through use because the next experiment with water gas gave a high yield.

The H_2 and CO_2 mixture had a composition of CO_2 27.6%, H_2 61.2%, CO 0.8%, CH_4 9%. It was interesting to note the formation of CO during the reaction. The exit gas comprised 4.3% CO. This suggested that the course of the reaction may have involved a primary reduction of CO_2 to CO as pointed out by Boomer and Morris (21).

At 350°C the conversion was 68.7%. There was no oil formation

observed in any of these experiments with this catalyst and the condensate was nearly pure MeOH. The conversion was 64% at 375°C. However the formation of CO₂ and a slight decrease in the value of CO were shown by the exit gas analysis. The low temperature activity of this catalyst was measured. It was found that at 275°C the percent conversion of CO to MeOH was 52%, but fell off very rapidly with the formation of small amounts of pure MeOH persisting down to 225°C. A number of other samples of this catalyst were prepared and at 300°C they gave high yields of pure methanol. This catalyst gave uniformly good results.

A Zn-Cu-Al catalyst with the constituents in the ratio 3: 2: 2 formed practically pure MeOH at 300°C but it soon lost its activity. The conversion was 35.7%. This value fell to 22.6% at 325°C and small amounts of impurities such as water were present. At 350°C the conversion was 14.6%, while at 400°C no evidence of reactions, except a small increase of CO₂ in the gas, was noticed. The composition of the inlet gas was CO₂ 1.4%, H₂ 60.6%, CO 28.4%, CH₄ 0.8%. Several other samples of this catalyst were tried at 300°C and few side reactions in the gas phase occurred as shown by a comparison of the gas analysis of Experiment No. 180 and the reactants. In this case the conversion was 62.7% after two previous runs had been made with the catalyst. Evidently this catalyst was very reactive but was easily damaged by heating above 300°C.

Catalyst No. 117 had a molar constitution of Zn-Cu-Al in the ratio of 2; 1: 1. One sample gave a conversion of 52.6% at 300°C

with a space velocity of 1000 but the values for other runs under similar conditions were 28.9%, 32.4% and 32.7% which seemed to be fairly representative. When the temperature was raised to 350°C small amounts of oil and water were shown by the distillation and large volumes of CO₂ and CH₄ were formed, while the percent of CO fell. The following reactions may have occurred



The catalyst was not carbonized and did not lose its activity. A large amount of liquid was formed at 400°C but it contained oil, water and only a small quantity of compounds boiling at the temperature at which methanol appeared.

With H₂ and CO₂ in Experiment No. 90, water was formed in which the usual Cu(OH)₂ precipitate settled out on standing. The reactions in the gas resulted in a drop in CO₂ from 27.6% to 24.2%, and in H₂ from 61.2% to 45.4%, while the CO increased from 0.8% to 5.2% and the CH₄ from 9% to 22.2%. In this case also it was assumed that one of the first steps in the reaction was the reduction of carbon dioxide to carbon monoxide. Subsequent reactions of the carbon oxides would account for the products. In Experiment No. 91 14% of the condensate separated out in an oil layer during an extended run at 350°C. A new sample of the same catalyst was

prepared; with it no oils were present in the liquid products and the amounts of CO₂ and CH₄ formed were uniformly small. The activity of this catalyst was moderately high and the synthesis of MeOH took place only at 300°C but the catalyst quickly deteriorated in use.

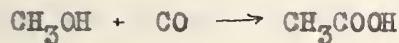
The first sample may have contained alkalies which would catalyse the reactions leading to CO₂, CH₄ and oils. It was noted that in no case was ethanol present. If we assumed that it could only be formed as a secondary product, for example, by the dehydration of the lower alcohol; then aluminium, which was known to be a dehydrating agent, was not sufficiently catalytic to carry out the reaction



The odor of dimethyl ether was not found in any case.

A new series of catalysts, which comprised the borates, phosphates and silicates of certain of the metals suspected of activity were investigated. With copper phosphate traces of acidic liquid were secured at 300°C and 450°C. No liquid products were given by two other phosphates and no deviation in the composition of the gas from the average could be discerned. No desired reactions took place over iron borate. Ordinary copper silicate, as well as the gels formed by the method of Holmes and Anderson, referred to above, were tried. They did not even promote reactions to gaseous products. Slight reactions did occur with the complexes of Zn-Cr-Si and Zn-Cu-Si, but they did not approach the

activity which would be expected from them. This series of catalysts should have been dehydrating but only the formation of small amounts of acids took place probably according to the reactions,



Two samples of different composition containing Zn-Co-Al were subjected to both gas mixtures. The one having the larger amount of cobalt present was the most active in the production of water. It should be noted that the CO_2 was not reduced to CO; hence no MeOH would be expected from H_2 and CO_2 mixtures over this catalyst, in Experiment No. 77 and 83. Tests showed that acids were present which in turn explained the precipitate of copper found on occasions.

An iron catalyst promoted by aluminium came next. At 300°C 60 c.c. of liquid were collected during the passage of 9.46 cu. ft. of gas from the apparatus. CO_2 and CH_4 were formed at the expense of the CO. 25% of the liquid was an oil boiling evenly over the range 60°C to 100°C . No change in the yield of oil occurred at the next temperature but at 400°C the yield of products was definitely lower than in the initial experiment as shown by a condensate of 20 c.c. of water, 3 c.c. of oil and 4 c.c. of an unidentified aqueous mixture. No MeOH was present. Hydrogen and carbon dioxide did not form oils or hydrocarbons to any extent in Experiment No. 150 and 151.

Nickel carbonate with a promoter of manganese was not reactive at 300°C, but at a higher temperature it formed 56 c.c. of water and a gas effluent of 6.52 cu. ft. which contained 73% of saturated hydrocarbon gases. The high yield of saturated hydrocarbons would suggest that the NiCO_3 was reduced to metallic Ni promoting the synthesis of hydrocarbons as pointed out by Fischer (1).

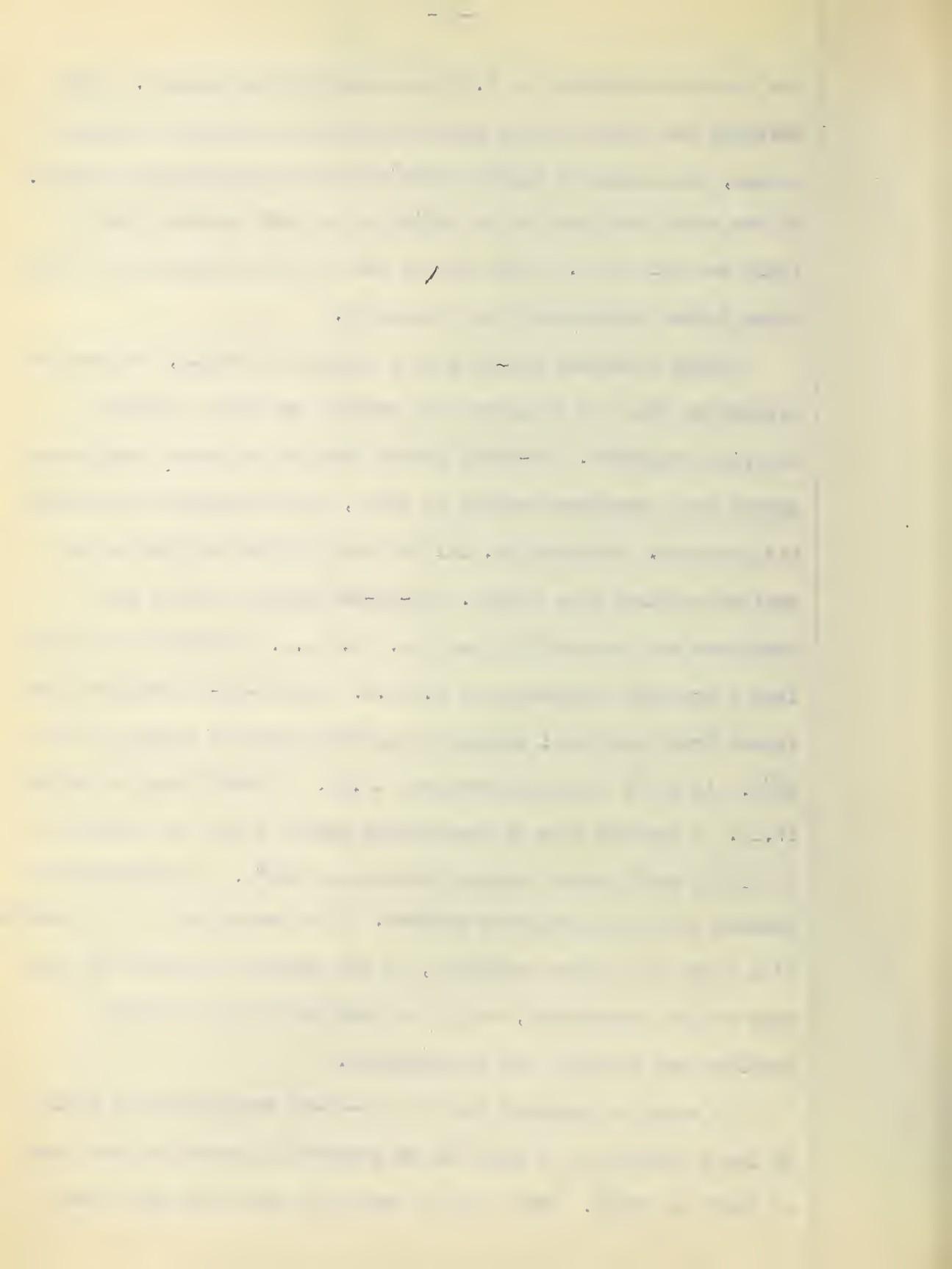
Four catalysts used by Morgan and co-workers (6), were next investigated. Catalyst No. 132 gave practically pure water. A trace of acetaldehyde and faint indications of formaldehyde were secured, but no test for ethanol. At a constant rate of flow and a higher pressure than usual, the temperature was varied over the range 300°C to 400°C. An Experiment, No. 164, using H_2 and CO_2 was conducted. This catalyst was found to be unreactive contrary to the results of Morgan showing both lower alcohols. With the Cu-Mn-Co 1: 1: 0.01 mixture only a few c.c. of liquid came from the reaction. The other Co-Mn-Zn catalyst promoted water formation equally well from water gas or hydrogen and carbon dioxide. Schiff's reagent did react weakly to show aldehydes but EtOH and higher alcohols were not present.

Experiments 204 to 208 inclusive employed basic zinc chromate and after two negative runs at low temperatures it gave MeOH at 350°C. The conversion was 18.2% to pure MeOH. No evidence of side reactions occurring in the gas could be found. When the temperature was raised to 400°C the conversion was still of the same order, 16.8%. A small amount of CO was lost to CO_2 . At 450°C

the conversion dropped to 7.9% and again CO₂ was present. This catalyst has been tried by many experimenters and particularly by Morgan, who worked at 350°C to 400°C and 200 atmospheres pressure. It has here been shown to be definitely a MeOH catalyst but the yield was only fair. This may be due to the low pressure at which these latter experiments were conducted.

Simple equimolar mixtures of a variety of metals, prepared as hydroxides from the nitrates were reduced and their catalytic activity estimated. Co-Cu-Al in two runs at the lower temperature showed that reactions leading to water, carbon dioxide and methane had occurred. Catalyst No. 121 had very little activity and no desired products were formed. Mg-Al-Mn did not promote side reactions and the activity was low. 2.5 c.c. of MeOH were secured from a combined condensate of 3.5 c.c. The Zn-Al-Mn catalyst also formed MeOH with small amounts of aqueous products boiling up to 80°C. At 300°C the conversion was 12.1%. At 350°C this value was 17.1%. A further rise in temperature caused a fall in conversion to 11% at 400°C and a further decrease at 450°C. No evidences for gaseous side reactions were noticed. By a comparison of the results with these two latter catalysts, it was assumed that zinc was the most active constituent, while the reaction over the former catalyst was probably due to manganese.

It would be expected that the Zn-Cu-Mn catalyst would build up large quantities of MeOH but no reaction appeared to take place at 300°C or 400°C. This lack of catalytic power may have been



due to the method of preparation and not to the nature of the constituents. Catalyst No. 128 was unreactive. The Zn-Fe-Cr mixture showed same activity at 350°C. 1.0 c.c. of MeOH, 1.6 c.c. of a clear oil and a complex aqueous mixture were secured from 20.5 c.c. of condensate. Carbonization probably occurred at 350°C and 400°C. Zn-Fe-Cu gave a maximum of liquid products at 400°C which consisted of water principally, oil and a small amount of MeOH. Methane and carbon dioxide were formed in large quantities.

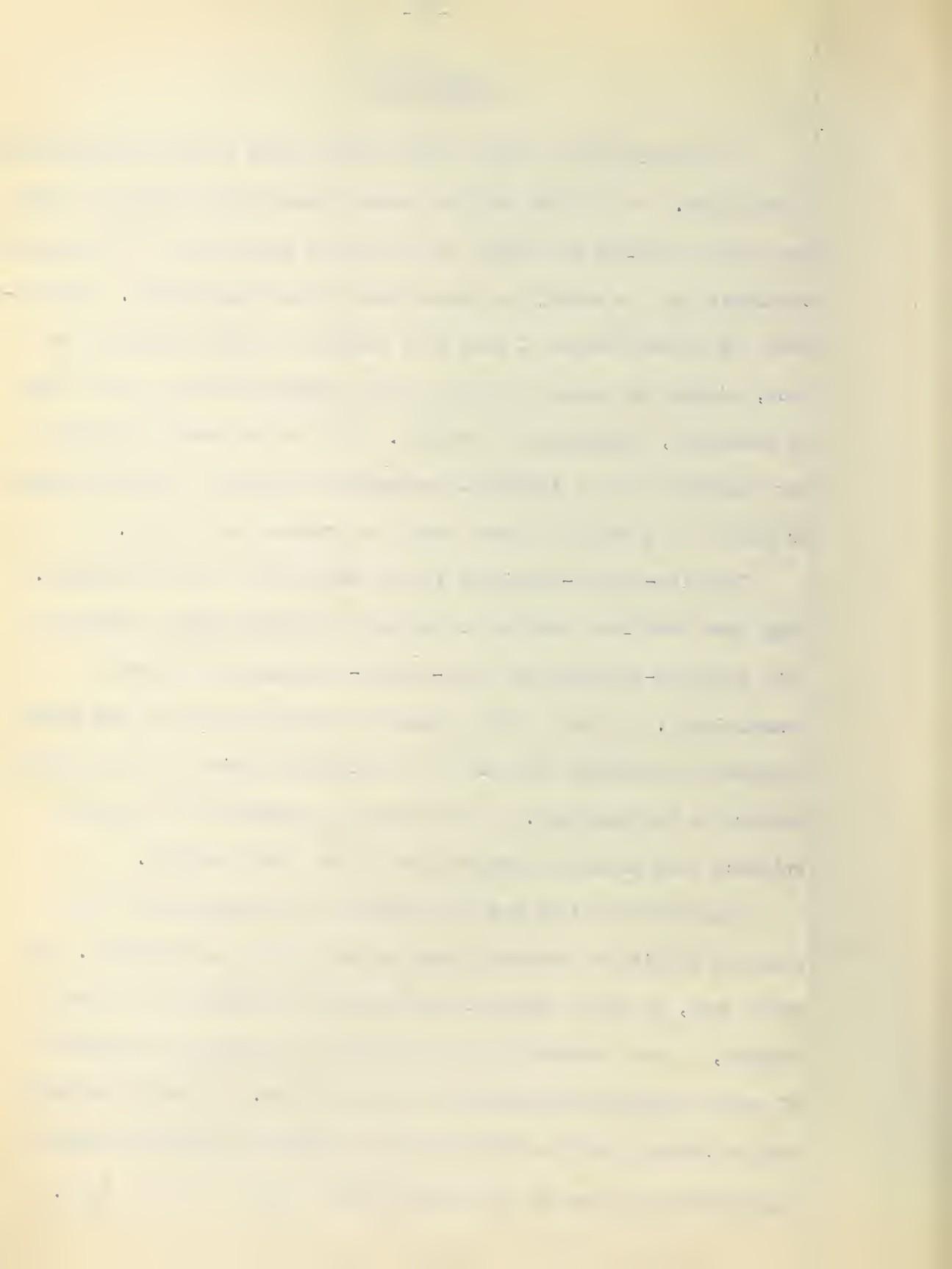
The Mg-Cu-Al catalyst gave 8 c.c. of MeOH with a measured exit gas flow of 1.55 cu. ft. of gas but at 450°C the yield had fallen to zero. The active constituent was undoubtedly the copper. The last catalyst in the table promoted no reactions.

DISCUSSION

A consideration of these results gives rise to very few positive conclusions. An obvious negative result lies in the failure to show any great correlation between the catalytic properties of these mixed catalysts and the catalytic properties of the constituents. Furthermore the effectiveness of such well known and active catalysts as iron, nickel and copper is very largely suppressed when in the form of silicates, phosphates or borates. This is not unexpected with the silicates but is definitely surprising with the others in as much as part of the metal at least would be expected to be free.

The zinc-copper-aluminium series exhibited the most interest. They show excellent results as methanol catalysts quite comparable with the zinc-chromium and zinc-copper-chromium series used commercially. In view of the absence of dimethyl ether or any other dehydration products the role of the aluminium oxide in the catalyst appears to be uncertain. It can only be concluded on the present evidence that alumina plays the part of an inert support.

Considerable light has been thrown on the mechanism of the reaction leading to methanol from carbon dioxide and hydrogen. In every case, in which methanol was formed from hydrogen and carbon dioxide, it was associated with water and a considerable quantity of carbon monoxide was present in the exit gas. It may be assumed that a primary reaction involving the reduction of carbon dioxide took place according to the equation $\text{CO}_2 + \text{H}_2 \longrightarrow \text{CO} + \text{H}_2\text{O}$.



Evidence for this reaction is given in Experiments No. 112, 151 and 90. In Experiment No. 162 no methanol was formed and no carbon monoxide was present in the exit gas. The subsequent reaction of carbon monoxide and hydrogen may take place through some intermediate compound formation or the gases may be adsorbed on the active centres of the catalyst surface where reaction may take place.

The mechanism of the reaction $\text{CO} + 2\text{H}_2 \longrightarrow \text{CH}_3\text{OH}$ has been the subject of considerable speculation. It is generally agreed that it is a complex reaction with formaldehyde or formic acid as an intermediate. In the light of some observations with the Zn-Cu-Al series, it is desired to propose a mechanism for the reaction occurring on the catalyst surface, that will account for the products.

It was observed that the clear condensate from the reaction of water gas over Zn-Cu-Al catalysts evolved gas slowly, commencing some time after the pressure on the liquid was released. The solution was practically pure MeOH in every case, it was colorless and neutral to litmus, while the precipitate tested qualitatively for copper only.

The liquid from the high pressure condenser of the apparatus for the methanol synthesis was quickly transferred to the burette of a micro gas analysis apparatus and the gas liberated was measured. It was possible to determine the CO_2 by passing 10% NaOH through the burette and allowing the gas to remain in contact

with the liquid for some time. Similarly bromine water and acid cuprous chloride removed unsaturated hydrocarbons and carbon monoxide respectively. The residue was mixed with air and exploded by means of a spark discharge between platinum wires sealed in the burette. In some cases, the liquid displaced a saturated salt solution in an ordinary gas sample tube. The evolved gas was then transferred to the standard gas analysis apparatus and the analysis carried out in the manner previously described.

T A B L E 3

Experiment No.	179a	191	184c	187a	180	184b	190
Volume of liquid c.c.	-	-	-	30	65	-	50
Volume of gas evolved c.c.	13.6	6.2		10	9.4	29.5	19.7
Gas Analysis %							
CO ₂	40	32	49	24.2	59.5	68	55
CO	23	41	16	66	17.0	13.2	17.5
H ₂	-	-	0	-	2.4	2	5
CH ₄	9	1.8	19	-	18	10	19
Unsaturates	-	-	3	-	3.1	6.2	3.3

The results are given in Table 3. The first four analyses were conducted with the small apparatus, the last three in the standard apparatus. The value of CH₄ for Experiment No. 180 is not accurate due to an explosion in the burette. An approximate

average composition of this evolved gas would be CO_2 55%; CO 16%; CH_4 18%; unsaturates 3%. The rate of evolution of gas varied widely. It was observed that the presence of traces of water in the condensate favored the rapid formation of gas, while the addition of water, dilute acids and alkalies speeded up the reaction. In one case No. 179b the condensate was boiled, water was added and a further evolution of gas took place. With CO_2 and H_2 mixtures, water is a product of the reaction. Although the precipitate was found, no gas evolution was noticed in these cases on removing the condensate. The water formed, no doubt, caused the decomposition to take place previously.

It is of interest to note that the precipitate was not copper but likely a hydrated oxide of copper, since it was readily soluble in dilute acids. Also the interior of the reaction chamber was covered with a fine copper dust that could be easily brushed off. The copper lining was not pitted as would occur had acidic products of the reaction attacked the walls of the reactor. In the absence of a catalyst, no reaction occurred, which demonstrated the inertness of ordinary copper metal. The solution was clear and neutral as well.

Mellor has pointed out that iron, nickel and silver formed carbonyls, which decomposed on heating to give the metal or its oxide and carbon monoxide. No evidence of this reaction between copper and carbon monoxide was known. Bertrand (22) passed carbon

dioxide over hot copper and the carbon monoxide formed was then passed over hot copper oxide. In the cooler part of the tube a mirror of copper was deposited. This suggested that some gaseous compound of CuO and CO, which was highly unstable, had been formed. Mond and Heberlein (23) repeated this experiment but found no evidence for the formation of a copper-carbon monoxide complex. Bartlett and Merill (24) found that copper and hydrogen reacted at 300°C to form cupric hydride, CuH₂, which gave off hydrogen when treated with water. The hydride is a good reducing agent but it is unlikely that it could carry out the reduction of carbon dioxide dissolved in the methanol to account for the carbon monoxide and methane present in the gas. Further, the amount of hydrogen was small in every case.

It is extremely difficult to account for the gaseous products. Carbon dioxide was known to be very soluble in MeOH under pressure, but the formation of gas from the liquid after boiling suggested that not all the evolved gas was dissolved in the condensate. The decomposition of a copper carbide may have taken place but CuC₂ and Cu₂C₂ are stable and only give off acetylene when treated with dilute acids. The small amount of unsaturates did not offer a full explanation of the phenomenon observed.

The formation of a copper carbonyl which may act as an intermediate in the synthesis of methanol is proposed. Such a compound formed with the copper atoms of the catalyst would present centres

of activity for colliding hydrogen molecules, and result in the formation of a copper-carbon monoxide-hydrogen complex from which methanol would be split off. That same evidence for the existence of a copper carbonyl has been found only on active methanol catalysts would support this mechanism of reaction. The absence of indications of a zinc carbonyl can be attributed to the greater attachment of the zinc oxide molecule to the catalyst than of the copper. The whole ZnO molecules would require removal since it is very unlikely that ZnO is reduced. Adsorption data given by Hoskins and Bray (32) on Zinc oxide and copper showed that carbon monoxide was adsorbed in preference to hydrogen. Apparently the first step is the adsorption of carbon monoxide which is followed by reaction with hydrogen.

SUMMARY.

An apparatus for the investigation of gas reactions over catalysts at high pressures and temperatures has been described.

The activity of some thirty catalysts has been investigated using water gas and hydrogen and carbon dioxide mixtures.

A new series of efficient methanol catalysts containing zinc, copper and aluminium has been found.

No relation has been found between the activity of a catalyst mixture and that of its constituents. It was not possible to predict the nature of the products of the reaction over a mixed catalyst from the data of the reaction over each constituent.

The isolation of ethanol has not been possible with the analytical methods employed, but condensation products such as oils have been found.

A new theory of the mechanism of methanol formation, by way of an unstable copper carbonyl intermediate, has been proposed.

It has been shown that the first stage in the formation of methanol from carbon dioxide and hydrogen consists of the reduction of carbon dioxide to carbon monoxide.

THE PROPERTIES OF TETRALIN AS AN HYDROGENATING CATALYST

Introduction

Some interest arose in connection with the compound tetrahydronaphthalene, commonly and hereinafter termed tetralin, because of results obtained in another series of researches. It was discovered in this latter series that tetralin was much superior to any other medium for the suspension of coal during its hydrogenation. The action was traced to the behavior of tetralin as a hydrogen carrier. It possesses the ability to a marked degree of accepting and giving up hydrogen easily. The resulting products are decahydronaphthalene and naphthalene in each case. In the temperature range of 250°^C to 400°^C and in the presence of hydrogen under pressure all three of these compounds are present in an equilibrium which is rapidly reached. Evidently tetralin plays the role of a hydrogenating catalyst. It differs from the others in that it is a definite chemical compound and the intermediate complexes are well known.

Experiments were carried out to determine the effectiveness of tetralin as a hydrogen carrier in the reduction of carbon monoxide by hydrogen or as an hydrogenating agent on carbon monoxide. This series of experiments was extended to include a

preliminary survey of the hydrogenating power of tetralin, and included the reduction of pure cellulose and wood to oils.

Literature review

No references to tetralin as an aid in the reduction of carbon monoxide by hydrogen was found in the literature. The hydrogenating powers of tetralin are well known in other respects, as pointed out by Ellis (33) from the patent literature.

A voluminous literature exists however regarding the thermal decomposition of cellulose and in a few cases hydrogenation under pressure has been undertaken. Waterman and Perquin (25) found that cellulose was decomposed to a black residue resembling coal at 325°C under atmospheric pressure. Carbon dioxide, water and methane were formed but if the temperature was raised to 450°C , carbon monoxide and hydrogen were also present and a solid residue corresponding to 37% of the cellulose was recovered. In the presence of hydrogen more hydrocarbons were formed and the reaction in a liquid medium of Borneo petroleum showed a decrease in the solid residue.

Bergius (26) decomposed cellulose thermally in a closed vessel under the pressure of the autogeneous gases and obtained a coal like substance, which was later hydrogenated to a liquid resembling a crude petroleum. Bowen, Shatwell and Nash (27) obtained tar, carbon dioxide, water and carbon monoxide by the pyrolysis of cellulose and a thick yellow oil by vacuum distillation. They found that cellulose did not undergo any appreciable hydrogenation at 440°C and a hydrogen pressure of 120 to 130

atmospheres. This reaction may have been inhibited by the carbonization which took place. Nickel was added as a catalyst and a 3 to 4% decrease in hydrogen pressure was noticed. Water, tar and a small amount of a light oil were recovered. The exit gas had an approximate composition of H₂ 84%; CH₄ 5%; CO 2.5%; CO₂ 8%. With a vanadium and an iron-vanadium catalyst a small adsorption of hydrogen was observed. Frolich, Spalding and Bacon (28) found only a small yield of oil and gas when cellulose was treated with hydrogen in the presence of a methanol catalyst. Similar results were noticed when nitrogen was used. This indicated that a thermal and not a hydrogenating reaction had occurred.

A number of papers have been published dealing with the distillation of wood at atmospheric and high pressures. Palmer (29) observed that gas was first formed in the destructive distillation of wood, then formic acid, acetic acid and later tar and methanol. Above 275°C methanol and acetic acid were decomposed to a certain extent. In an earlier paper an increase in methanol was noticed when the reaction was carried out at 335°C in the presence of hydrogen.

Frolich, Spalding and Bacon (28) set forward the results of an investigation conducted to increase the yield of methanol from wood. Heating wood in a closed reactor at 280°C to 370°C developed a pressure of 100 atmospheres and caused an increase of from 65 to 80% in the yield of methanol. Higher temperatures decreased the amounts

of liquid products and seemed to favor the formation of methane. Reactions with hydrogen under pressure gave 100% increase in methanol over that found at atmospheric pressure. The actual yield was 3.11 g. of MeOH per 100 g. of wood. Wood impregnated with methanol catalysts and hydrogenated under pressure gave poorer yield of MeOH than similar experiments with no catalyst. Increased amounts of tar were produced when the catalyst was present. As expected, nickel caused a marked increase in the methane content of the gas.

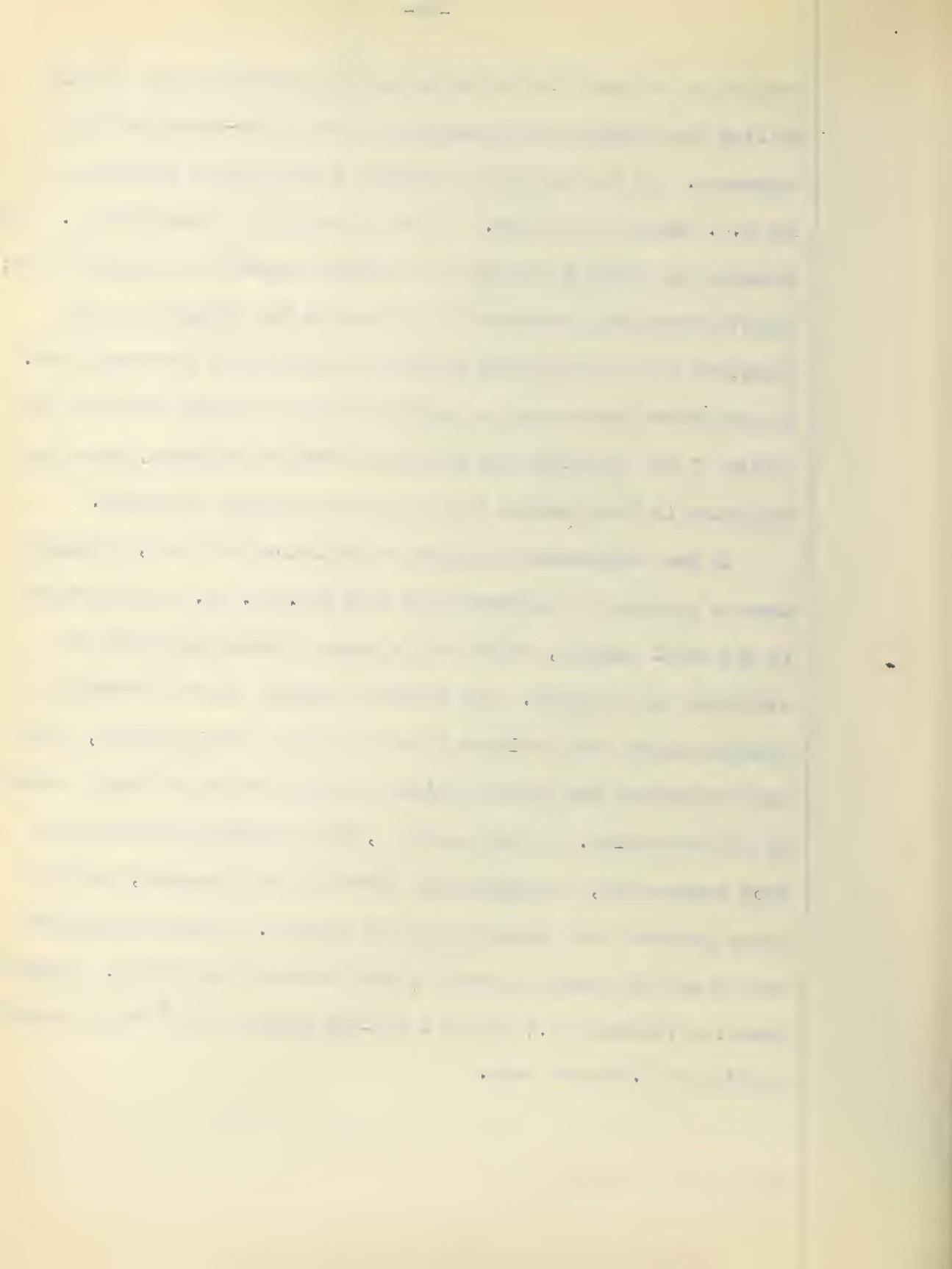
Wood was hydrogenated under pressure in the presence of various catalysts by Lindblad (30), who found that nickel or cobalt catalysts resulted in the formation of a thick tar at 250°C. Methane was formed at higher temperatures. Sawdust impregnated with cobalt sulphide was hydrogenated and resulted in a large hydrogen adsorption at 350°C, with the formation of oils amounting to 40% of the weight of the wood. Cupric hydroxide, molybdic acid and zinc chloride also gave good results. Sulphite liquor was used as a carrier and with ferrous hydroxide it formed ferrous sulphide, which gave better results than ferrous hydroxide alone. Fifty-eight percent of the weight of the carbonized charge was recovered as oil, while an amount of hydrogen equivalent to 5.5% of the weight of the charge was absorbed during the reaction.

Experimental

The gaseous and liquid products were analysed as has been described previously. The recovery of tetralin from the reaction was

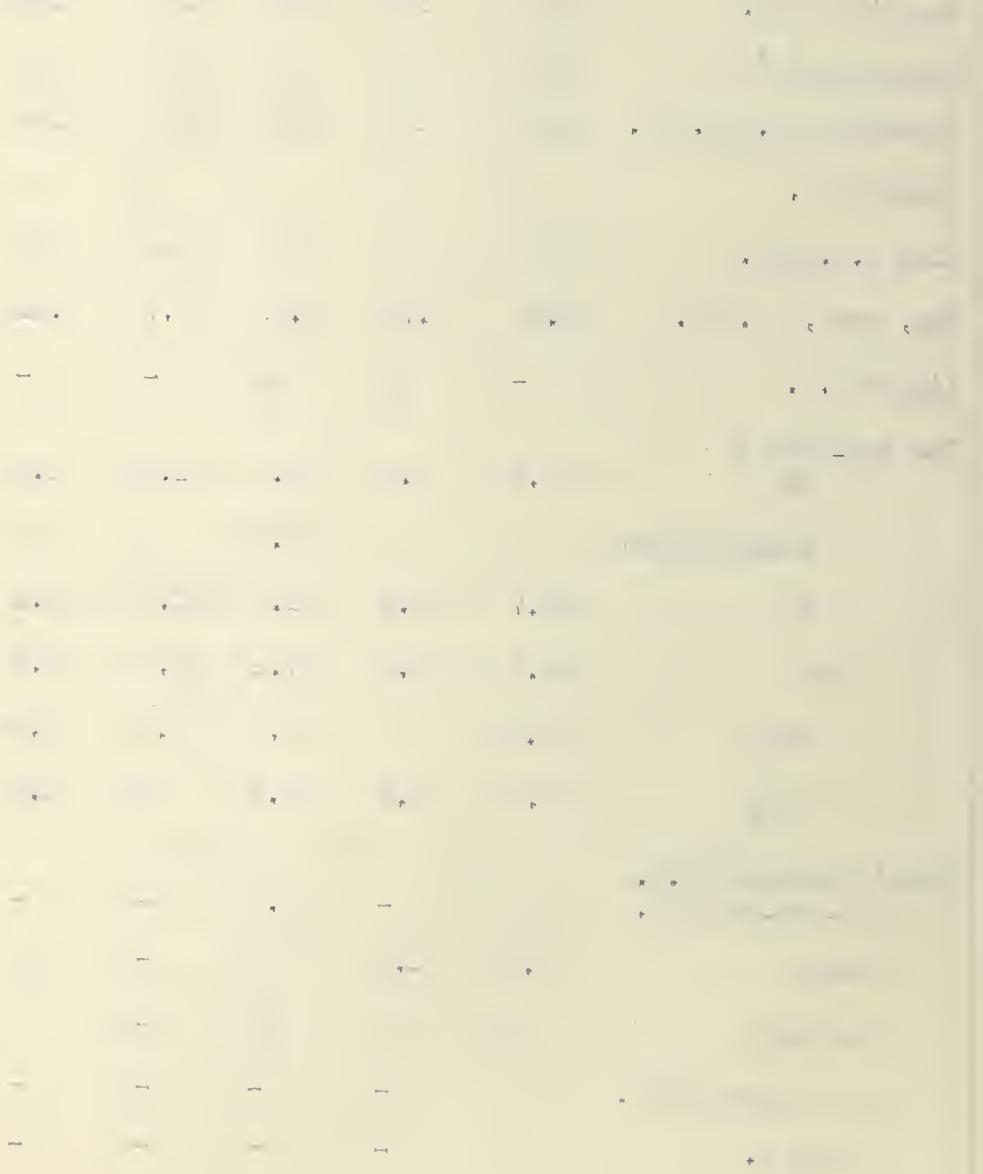
carried out by distillation using an air condenser after the low boiling constituents were recovered in the micro-fractionating apparatus. In the water gas reactions a small steel reactor of 180 c.c. capacity was used. It was fitted with a glass lining. The incoming gas bubbled through the tetralin placed in the glass liner; but otherwise the arrangement of apparatus was similar to that described in the preceding reactions of water gas over catalysts. In the latter experiments an upright copper tube was fitted to the outlet of the autoclave and acted as a reflux condenser, preventing the tetralin from passing over into the receiving condenser.

In the experiments conducted on cellulose and wood, hydrogen under a pressure of approximately 1000 lbs./sq. in. was introduced to the small reactor, which held a glass thimble containing the cellulose and tetralin. The reaction chamber and the recording pressure gauge were isolated from the rest of the apparatus, while the temperature was quickly raised to that desired and kept constant by the controller. After reaction, the autoclave was cooled to room temperature, the gases were drawn off and analysed, and the other products were removed from the reactor. Ordinary absorbent cotton and fir sawdust served as the sources of materials. Practical tetralin (Eastman Co.) having a boiling point of 206° C and a specific gravity of 0.925 was used.



T A B L E 4

Experiment No.	182	183	186	188	189
Temperature °C	200	200	200	200	200
Pressure lbs./sq. in.	2400	2100	2250	2350	2150
Catalyst g.	0	0	0	4	9
Flow c.c./min.	1400	800	460	340	600
Gas, exit, cu. ft.	4.82	4.73	4.59	2.7	6.11
Liquid c.c.	-	63	61	-	-
Gas Analysis %					
CO ₂	0.8	0.6	0.8	1.0	1.9
Unsaturates	0	0	0.3	0	0
H ₂	63.7	63.2	61.4	61.6	61.1
CO	25.8	24.5	27.1	27.0	26.2
CH ₄	0.4	0	3.5	4.8	0.85
C ₂ H ₆	2.5	2.9	0.3	0	1.9
Liquid Analysis c.c.					
Oil below 95°C.	2	-	0.5	-	-
Water	1.2	1.4	0	-	5
Tetralin	65	+	60	+	+
Oil above 205°C.	+	-	-	-	-
Pitch g.	+	-	-	-	-



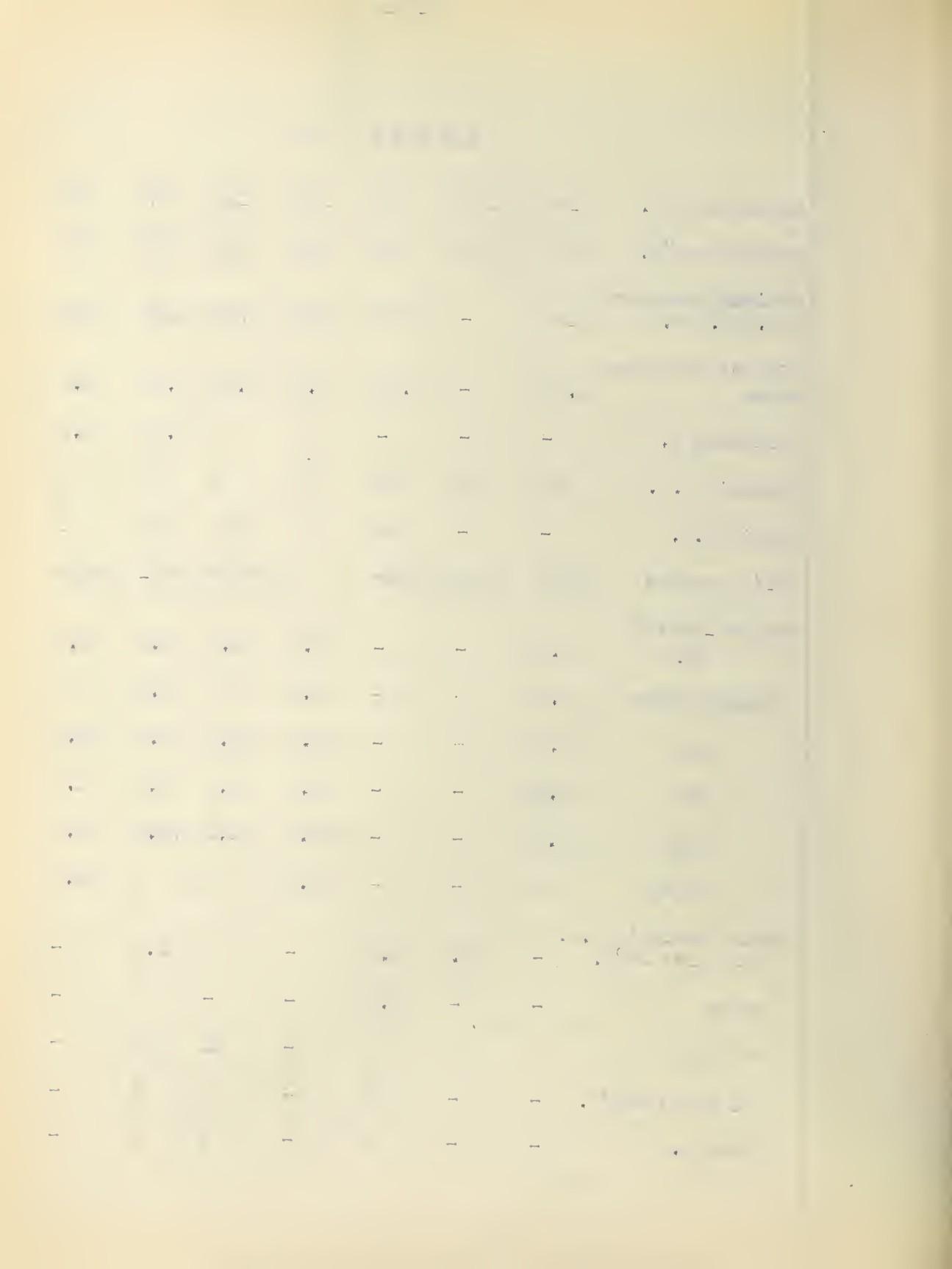
Experimental Results

The results with carbon monoxide and hydrogen gas mixtures are given in Table 4. In the first experiment 4.82 cu. ft. of water gas was passed through the tetralin solution at 2400 lbs./sq. in. pressure and 200°C. A small amount of liquid was formed. Iron carbonyl was present and decomposed on distillation leaving a milky white precipitate in the liquid. No appreciable change in the composition of the gas occurred. The next run was made at a lower space velocity. 1.4 c.c. of aqueous products were formed but no ethanol or aldehydes were present. In Experiment No. 188, 4 g. of a methanol catalyst in a powdered form were mixed with the tetralin. A leak in the reactor prevented the recovery of the liquid but little change was noted in the composition of the gas during the reaction. 9 g. of catalyst were used in the last experiment and 5 c.c. of water were formed along with a small amount of carbon dioxide.

The experiments, in which cellulose was investigated, are summarized in Table 5. Reactions commenced at 200°C. Traces of carbon dioxide and methane were found in the gases but the charge was only slightly carbonized. On raising the temperature to 250°C, the cellulose became charred but retained its original physical form while a trace of oil and 3 c.c. of tar were produced. At 300°C a maximum pressure of 2250 lbs./sq. in. was developed. The cellulose was completely broken down and a heavy oil recovered. This oil showed 1.3% boiling below 100°C; 5% water; 7.5% heavy tar

T A B L E 5

Experiment No.	192	193	194	195	196	197	198
Temperature °C.	200	250	300	350	350	350	350
Maximum pressure lbs./sq. in.	1185	-	2250	2800	2775	4150	3600
Time of reaction hours	1.25	-	2.15	2.5	2.66	2.66	2.0
Cellulose g.	-	-	-	8	0	8.05	11.9
Tetralin c.c.	50	50	50	50	0	60	0
Liquid c.c.	-	-	40	0	50	60	1
Solid residue	Large	Large	Trace	0	Trace	Small	Large
Gas Analysis %							
CO ₂	0.6	-	-	4.9	1.2	4.9	8.2
Unsaturates	0.2	-	-	0.2	0	0.4	0
H ₂	96.5	-	-	87.6	95.3	6.6	85.8
CO	0.6	-	-	2.0	0.4	3.4	1.8
CH ₄	1.5	-	-	2.0	1.1	78.9	2.0
C ₂ H ₆	0	-	-	1.0	0	0	1.8
Liquid Analysis c.c.							
Oil below 95°C.	-	0.5	0.5	-	3	1.5	-
Water	-	-	0.2	-	-	2	-
Tetralin	+	+	+	-	41	39	-
Oil above 205°C.	-	-	3	-	3	7	-
Pitch g.	-	-	+	-	2	3	-



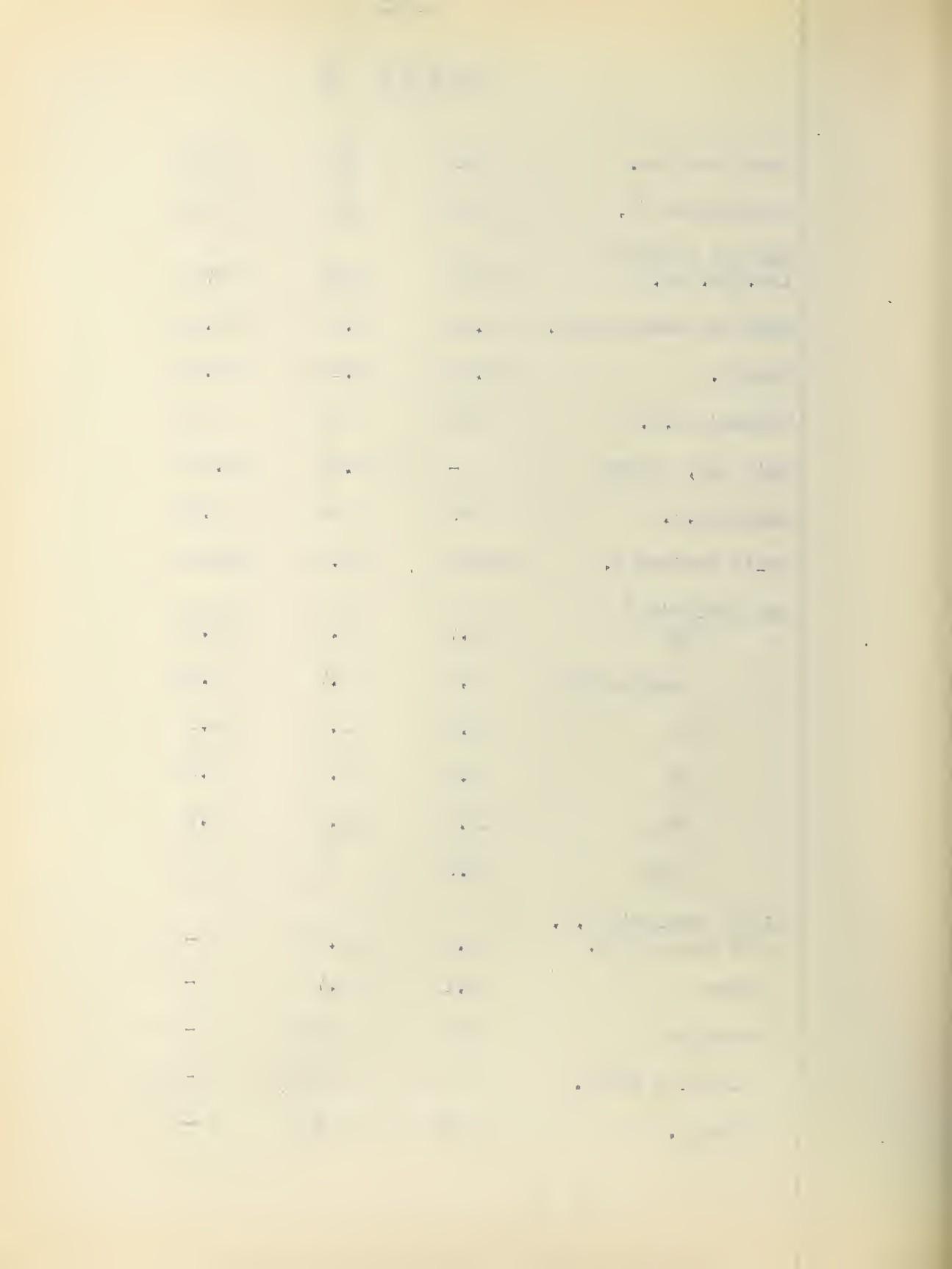
and the remainder consisted of tetralin with a small residue of coke. A leak developed in the plug at the bottom of the steel cylinder during cooling, so that no gas sample could be taken.

In Experiment No. 195, 8 g. of cellulose and 50 c.c. of tetralin were placed in the reactor and a two cycle run commenced at 350° C. The presence of CO₂, CO, CH₄ and only 87.6% H₂ in the exit gas suggested that some reaction had taken place. A fresh sample of hydrogen was used and in this case 95% of the H₂ was found in the exit gas. Hence the first reaction must have been the most vigorous. Oil, tetralin and coke were calculated as shown in the table.

In order to show that the tetralin was taking a part in the reaction an experiment was tried in which methane was used in place of hydrogen as the gas phase. Any hydrogenating reaction by the tetralin would be shown by the presence of naphthalene in the products. The cellulose was disintegrated, unsaturated hydrocarbons were noticed along with CO₂ and CO, and only 65% of the tetralin was recovered with 2 g. of naphthalene. In Experiment No. 198, cellulose was heated at 350° C with hydrogen alone up to a maximum pressure of 3000 lbs./sq. in. The cellulose was charred somewhat, but not greatly broken down in that it retained its physical structure. The presence of carbon dioxide was probably due to the thermal decomposition of the cellulose, while subsequent reaction of CO₂ and H₂ may have produced CO and CH₄.

T A B L E 6

Experiment No.	199	200	201
Temperature °C.	350	350	350
Maximum pressure lbs./sq. in.	3850	4050	2275
Time of reaction hrs.	3.16	3.5	2.0
Wood g.	18.55	15.16	15.2
Tetralin c.c.	60	60	0
Exit gas, litres	-	10.92	10.65
Liquid c.c.	69	65	0.3
Solid residue g.	Trace	2.5	Large
Gas Analysis %			
CO ₂	22.7	6.4	12.2
Unsaturates	0.5	0.7	0.4
H ₂	53.0	1.9	74.9
CO	5.4	4.3	2.9
CH ₄	12.6	84.8	9.7
C ₂ H ₆	2.9	0	0
Liquid Analysis c.c.			
Oil below 95°C.	2.5	1.5	-
Water	4.1	2.7	-
Tetralin	50	49	-
Oil above 205°C.	6	5	-
Pitch g.	+	2	-



All hydrogenation reactions with wood were carried out at 350°^oC. In the first case 18.55 g. of wood and 60 c.c. of tetralin gave large amounts of CO₂, CO, CH₄ and C₂H₆, with only a small amount of coke remaining in the reactor. Comparatively large amounts of aqueous and oily liquids were obtained as shown in Table 6. With methane in place of hydrogen, it was found that the hydrogenation of wood could be carried on with the limited supply of hydrogen given out by the breakdown of tetralin to naphthalene; but the reaction was not as complete as in the former case. 4.5 g. of naphthalene were recovered. A third experiment was studied with no tetralin present. A considerable adsorption of hydrogen took place but the wood was not completely broken down, the greater part being left in the reactor after the experiment, while the gaseous products were not formed in as large an amount as in the first run. Only a small quantity of liquid was secured.

Discussion

It is evident from the experimental data that tetralin has little or no power as a catalyst in the reduction of carbon monoxide by hydrogen at 200°^oC. Even the addition of an active methanol catalyst did not promote the reaction appreciably. The test is not however conclusive in view of the low temperature used. No heterogeneous catalyst is known that has any great activity below 225°^oC and it would be extremely surprising if tetralin proved effective under these conditions. The subject is worth more investigation.

The hydrogenation of cellulose did not proceed to any appreciable extent below 350°C and the charge was not fully decomposed; but definite proof that a reaction yielding liquid and gaseous products occurred at 350°C, was shown in the two cycle experiment. Further it was shown, that with tetralin alone there was nearly as complete a reaction as with hydrogen present, and that tetralin was necessary in order to secure a complete reaction at this temperature.

Tetralin acted as a very efficient catalyst in the experiments on wood, promoting the formation of large amounts of carbon dioxide, carbon monoxide, methane, water and oils; while with hydrogen also present increased conversions to liquids and gases were shown to occur. Without tetralin there was some reaction but the decomposition of wood was less complete. It is clearly evident that tetralin is an effective agent in the hydrogenation of cellulose and wood, promoting oil formation and lessening coke production. Generally the presence of tetralin reduced the solid residue from the hydrogenation of cellulose to a negligible quantity. Almost complete reduction to liquids and gases was possible with tetralin as compared to very little reduction in its absence. The same conclusion may be drawn with regard to wood although the solid residue appeared to be somewhat greater than with cellulose. The nearly complete dissolution of wood is in sharp contrast to the results of other investigators.

PART 11

Preliminary experiments on the solubility of methane in hexane
at pressures to 250 atmospheres.

April, 1932.

GEORGE H. ARGUE.

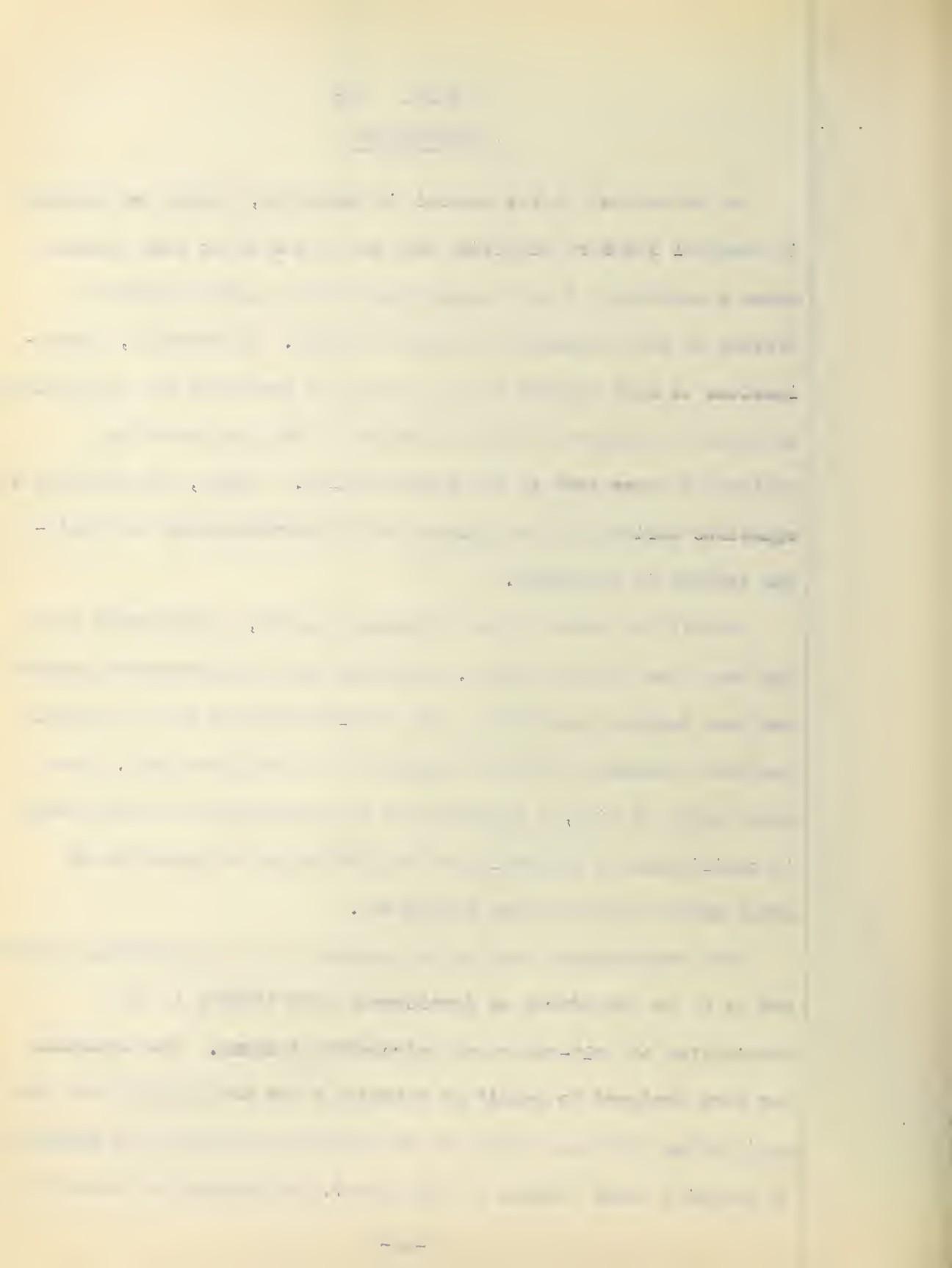
P A R T 11

INTRODUCTION

As emphasized in the general introduction, recent developments in chemical industry involving the use of gas under high pressure makes a knowledge of the compositions of two phase liquid-gas systems at high pressures of great interest. In addition, investigations of such systems as that one to be described are of peculiar interest in relation to the conditions in the gas producing horizon of areas such as the Turner Valley. Lastly, the checking of equations derived by the application of thermodynamics to liquid-gas systems is necessary.

As will be shown in the literature review, considerable work has been done on the subject. Previous work on hydrocarbon systems has been largely carried out with complex mixtures and in general has been concerned with the composition of one phase only. From every point of view, a knowledge of the composition of both phases in equilibrium is desirable and the derivation of equations of state makes such knowledge obligatory.

The experimental work to be reported is of a preliminary nature and is to be considered as development work leading to the examination of poly-component hydrocarbon systems. The apparatus has been designed to permit of bringing a gas and liquid phase into equilibrium with each other and to permit the recovery and analysis of definite known volumes of each phase. The components chosen were



purified Viking natural gas and hexane. Viking gas was chosen as the most convenient supply of methane and contains slight amounts of nitrogen and ethane. These components of widely separated boiling points allowed the use of simple analytical procedure, and were of sufficient purity for preliminary work.

THEORY

A complete treatment of the system considered is not at present justified. Sufficient data of the required accuracy is not available and no worth while purpose would be served by a complete treatment. Consequently an approximate treatment only is applied to the results and the general equations indicated.

It has been customary to calculate the vapour content of indifferent gases in contact with a liquid by assuming the application of the perfect gas law and a negligible solubility of gas in liquid. If p be the vapour pressure of the liquid in contact with a gas at pressure P at the temperature T :

$$(\text{Volume \% of vapour})_T = \left\{ \frac{100}{P + p} \right\}_T$$

In general p is small compared to P and the expression can be written without appreciable error;

$$(\text{Volume \% of vapour})_T = \left\{ 100 - \frac{p}{P} \right\}_T$$

If a portion of the gas phase be removed and allowed to expand the percentage of vapour will not change so that the above expression will hold for the expanded gas. This is obviously true only when the gas is a perfect gas. For real gases a correction must be applied and is most conveniently done by expressing the deviation from the perfect gas law by the ratio PV/P_0V_0 . This correction need not be applied to the vapour because of its low partial pressure. The

equation now becomes;

$$(\text{Volume \% of vapour in expanded gas })_T = \left\{ \frac{100 P}{P} \left(\frac{P V}{P_0 V_0} \right)_P \right\}_T \quad (1)$$

A further correction becomes necessary for two reasons. The gas is appreciably soluble in the liquid and in the ideal case will cause an alteration in the vapour pressure of the liquid calculable by Raoult's law. Also, the liquid has an appreciable compressibility which will result in a change of vapour pressure in the opposite direction to that predicted by Raoult's law. In the ideal case of a gas insoluble in a liquid, Poynting (34) has shown that

$$\left\{ \frac{dp}{dP} \right\}_T = \left\{ \frac{V}{v} \right\}_T$$

where V is the molal volume of the liquid and v that of the gas. This equation may be integrated readily on expressing V as a function of the pressure P and the compressibility and by applying the perfect gas law to the vapour.

$$\begin{aligned} V &= V_0 (1 - BP) \\ v &= RT/p \\ \frac{dp}{p} &= \frac{V_0}{RT} (1 - BP) dP \\ \ln \frac{p}{P_0} &= \frac{V_0}{RT} (P - P_0) \left(1 - \frac{B}{2} (P + P_0) \right) \end{aligned} \quad (3)$$

This calculation has taken no account of the operation of Raoult's law. An approximate method consists in using in place of p_0 the vapour pressure of the pure liquid at the temperature of the experiment a corrected value, p_0^l , calculated from the known composition of the liquid phase from Raoult's law;

$$p_0^l = N_1 p_0$$

where N_1 is the mole fraction of solvent in the solution. This assumes the application of Raoult's law to the present systems which is certainly not correct. However, until more precise data becomes available, an exact treatment becomes impossible.

The fundamental equation becomes, on taking into account the last two corrections;

$$\begin{aligned} & (\text{Volume \% of vapour in expanded gas})_T \\ &= \left(\frac{100}{P} \frac{p_0^l}{(P_0 V_0)} \right)_P \frac{p}{p_0^l} \Bigg)_T \quad (4) \end{aligned}$$

where p is the vapour pressure of the solvent at P and p_0^l is the calculated vapour pressure of the solvent at $P = p_0^l$ and mole fraction N as found by experiment at P . The ratio p/p_0^l can be obtained from the previous equation given a knowledge of the partial molal volume V_0 of the solvent in the liquid phase and its coefficient of compressibility B . The value of V_0 may be obtained from the analytical measurements, but B is unknown. For the present approximate treatment B will be taken

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as the same as that for pure hexane.

A general treatment leading to the fundamental differential equation is as follows. For the solvent in the liquid phase;

$$dF_1 = V dP + \frac{dF_1}{dc} dc$$

where F_1 is the partial molal free energy of the solvent and c is its concentration. For solvent vapour in the gas phase;

$$dF_2 = v dp$$

At equilibrium; $dF_1 = dF_2$

Hence $V dP + \frac{dF_1}{dc} dc = v dp$

$$V dP + RT d \ln a = v dp \quad (5)$$

where a is the activity of the solvent in the liquid phase expressed as a mole fraction. The integration of this equation requires an expression for V and for a in terms of P and for v in terms of p . Assuming an ideal solution and the application of the perfect gas law;

$$v = \frac{RT}{p}$$

$$a = N_1$$

$$d \ln a = d \ln N_1 = -d \ln N_2$$

$$N_2 = k P \text{ (Henry's law)}$$

Then $d \ln N_2 = d \ln P$ where N_2 is the mole fraction of solute.

$$\text{Therefore } V dP - RT d \ln P = RT \frac{dp}{p}$$

$$\frac{R T}{P} = v_2 \quad \text{where } v_2 \text{ is the volume of gas.}$$

$$\text{Hence } (V - v_2) d P = R T d \ln p$$

The integration of this equation requires an expression for V and for v_2 in terms of P. The value of v_2 may be readily obtained from the equation of state for the gas used and V only by compressibility measurements on the liquid. The assumption of Henry's law probably involves an error greater than that involved in using the ideal value of v_2 or the apparent value taken for V previously. Until more data are available no improvement is gained by developing Equation (5), above, over the previous treatment given.

LITERATURE REVIEW

The published material on the solubility of gases in liquids is very extensive and covers pressures to 1000 atmospheres and temperatures to 250°C. Tables of critical data have appeared recently (35) and a general review of the whole subject has been given by Hildebrand (36). A qualitative discussion of the consequences of the mutual solubility of liquids and gases by Freeth (37) emphasizes the necessity for more investigation.

Much of the earlier work was theoretical and dealt with phase rule considerations. The special case of a gas insoluble in the liquid has already been given (34). The general case of bivariant liquid-gas systems has been fully considered in the writings of Roozeboom and of Le Chatelier. On the experimental side the work of Harnay and Hogarth (38) covered a variety of systems to high pressures in which the gas was only slightly soluble in the liquid. The classic experiments of Villard (39) covered the increase in vapour pressure of bromine under 200 atmospheres pressure of hydrogen and oxygen. He states clearly the conception of the solubility of a liquid or a solid in gases at high pressures. Quantitative studies have been made by Sander (40) on the ethyl ether-carbon dioxide system; by Pollitzer and Strelbel (41) on water and air, and by McHaffie (42) on sodium sulphate-air systems at the transition point of the sulphate. Larsen and Black (43) have determined the solubility of nitrogen and hydrogen in liquid ammonia up to 1000

atmospheres, and more recently, Bartlett (44) has examined quantitatively the solubility of water in compressed nitrogen, hydrogen and their 1 : 3 mixture. These investigations have been concerned only with the composition of one phase and have not shown even qualitative agreement with Equation (1) combined with Equation (3) given previously. In general, the effect of pressure has been to increase the vapour content of the gas phase more than can be accounted for by these equations. Henry's law failed at comparatively low pressures, the amount of gas in solution being less than that predicted by the law.

Of less precise work, that of Krase and Goodman (45) on the solubility of water in compressed nitrogen and of carbon dioxide in water may be mentioned. The chief interest attached to the solubility of carbon dioxide in water at high pressures lay in the greatly increased acidity of the solution compared to the acidity of carbon dioxide solutions at atmospheric pressure.

The solubility of hydrocarbon gases in hydrocarbon liquids at ordinary pressures has been carried out by McDaniel (46) and his paper gives the essential references to earlier work. Frolich and collaborators (47) have examined in an approximate fashion the solubility of methane in various liquids, including saturated hydrocarbons, to 200 atmospheres. Within their limit of error, at least 5%, the results confirm Henry's law in that the amount of gas dissolved is proportional to the applied pressure. Bahlke and

Kay (48) have carried out a comprehensive examination of the P-V-T relations of petroleums and distillates above and below the critical region in a modified Andrew's apparatus. They were not able to obtain the composition of either phase but do give useful equations of state for their very complex mixtures. Methods of calculation of the thermal properties of petroleum and distillates, under conditions, such as occur in refining processes, are given.

The investigations of Dow and Reistle (49), Beecher and Parkhurst (50) and of Dow and Calkin (51), on the solubility of natural gas in various petroleums are of direct application in regard to producing oil wells. They showed in general that dry natural gas was soluble in petroleum to an amount proportional to the pressure. No satisfactory conclusions regarding the actual conditions in an oil well could be drawn. Further work by Mills and Heithecker (52) gave the solubility of dry natural gas and the volume and gravity changes in various petroleums up to 1000 lbs. per sq. in. Selective solution of the heavier constituents in the natural gas was evident but the proportionality between solubility and pressure was maintained. No data on the composition of the gas phase in equilibrium with the liquid was given. They conclude that further work is necessary in order to obtain a knowledge of the conditions at the bottom of a producing oil well. Lindsly (53) has extended the above work to 1700 lbs. per sq. in. and improved the experiments to make the results comparable with actual oil well operation. His liquid-gas systems were taken directly at the well

head, so that the natural gas used was identical with that occurring in the well and was as a consequence not a dry gas. His crudes include one light Kettleman Hill's oil that is roughly comparable with Turner Valley naptha. Lindsly failed to find even an approximate proportionality between pressure and solubility and showed by consideration of selective solubility and the assumption of Henry's law that this was to be expected. The composition of the gas in solution was determined by fractional distillation. In one instance the composition of the gas phase was determined and showed about 15% of hydrocarbons higher than methane as compared to 35% in the case of the gas in solution. The dissolved gas liberated at 1700 lbs. contained 0.485 gals. of pentanes and heavier per 1000 cu. ft. and the gas not in solution contained 0.411 gals. Of the total gas liberated at this well, 95.4% was not in solution in the oil.

EXPERIMENTAL

Materials

The materials used in the experiments to be described were Viking natural gas and a sample of n-hexane labelled "chemically pure".

The natural gas was of the composition;

CH ₄	92.4%
C ₂ H ₆	1.4%
C ₃ H ₈	0.9%
CO	0.15%
N ₂	5.15% (difference)

Its composition after purification in the manner to be described was determined by slow combustion with oxygen over a heated platinum spiral. The average of a large number of determinations gave the composition;

C ₂ H ₆	2.6 ± .6
CH ₄	95.1 ± .8
N ₂	2.2

The hexane was distilled in a 14" spiral packing fractionating column with a 2 to 1 reflux ratio. The initial boiling point was 62.6°C at 692 m.m. mercury pressure. Approximately 33% came over between 65°C and 67°C. This hexane is undoubtedly a mixture of isomers and probably less than 30% n-hexane. The fraction used in all this work was that boiling between 65.0°C and 67.3°C. At 692 m.m. of mercury n-hexane has a boiling point of 65.9°C.

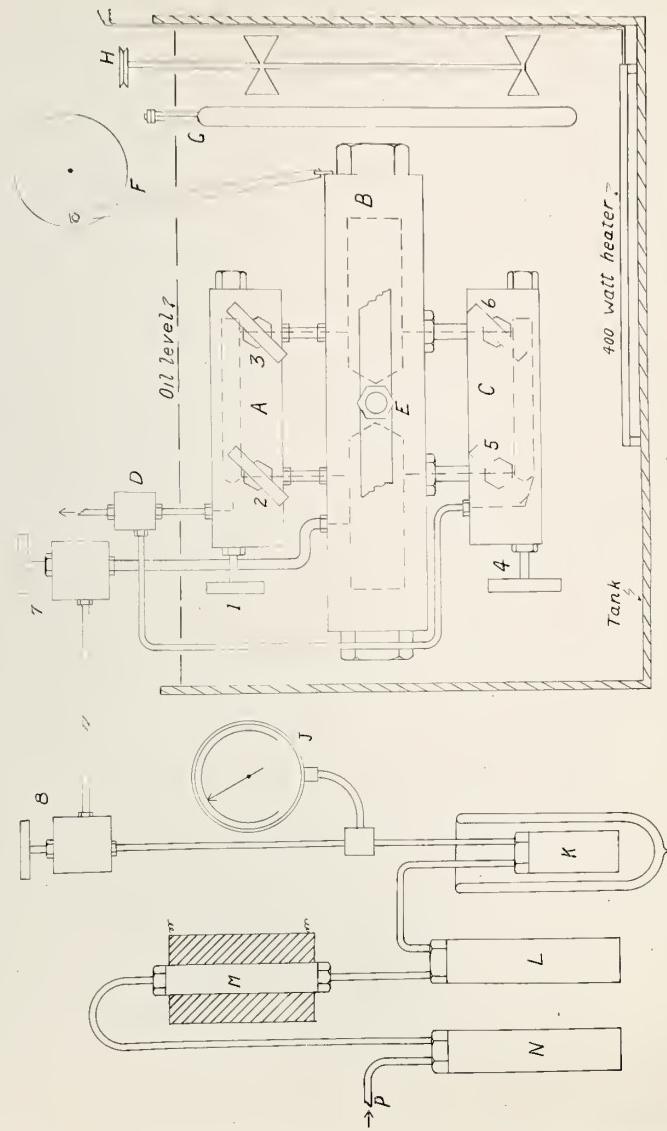
Apparatus and Operation

The apparatus consisted essentially of two parts; the steel solubility pipette and the gas supply system for the operation at high pressure, and the glass analytical system in connection.

The gas supply system and the solubility pipettes are shown in Figure 3. The solubility pipettes had to be of such design that equilibrium between the gas and liquid was reached at a reasonable rate and at equilibrium, provision had to be made for the withdrawal of known volumes of each phase. Obviously freedom from leaks at all operating pressures was essential. The rapid attainment of equilibrium could only be secured by some method of agitation. The mechanical difficulties associated with securing a gas tight gland made mechanical stirring unsatisfactory. A magnetic stirrer totally enclosed within the apparatus was possible but costly. The method chosen and found to work with entire satisfaction consisted of oscillating the solubility pipettes as a whole at a slow rate through a large angle.

Referring to Figure 3, the gas phase pipette is shown at A, valve 1 acted as a sampling valve and valves 2 and 3 permitted the isolation of the pipette A from the central reservoir pipette B. The pipette A had the approximate dimensions, $\frac{1}{2}$ " diameter by 4" depth. It was connected to the valve seats by $1/16$ " channels and when all valves were closed no possibility of a leak existed. The volume, including the passages as far as the valve seats with the valves closed, was determined by weighing the mercury required to fill the pipette.

FIGURE (3)



The volume was found to be 11.255 c.c. \pm 0.005 c.c. No corrections for the expansion of the pipette under pressure were necessary. An approximate calculation, by the method outlined by Keyes (54), showed a change in volume of less than 0.005 c.c. at 200 atmospheres. Pipette A was connected at each end by 1/16" by 1/4" steel tubing to the two chambers of reservoir B. This central reservoir was divided into two chambers each 1 $\frac{1}{4}$ " in diameter and about 4" long. Each chamber was approximately 60 c.c. in volume. Gas was admitted to B through the valve 7 leading from the purifying system and the pressure gauge. Each chamber in B was in communication with the lower liquid phase pipette C by 1/8" passages. The lower pipette C was similar to A but larger. All passages were of 1/8" diameter except those to the sampling valve 6 which were 1/16". The pipette proper was 5/8" in diameter and 21.028 c.c. in volume. Valve 5 and 6 enabled the isolation of pipette C from the central reservoir during withdrawal of the sample through valve 4. The passage from the pipette proper to the valve seat was drilled to enter the pipette at its lowest point, ensuring nearly complete removal of liquid during withdrawal under the pressure of the dissolved gas. All passages and chambers within the pipette proper are shown in the figure as dotted lines. The tubing of 3/16" copper from the sampling valves 1 and 4 led to the three way union D. A piece of 3/16" copper tubing leading from this union to a steel to glass ground joint connected the pipettes with the analytical apparatus,

when necessary. Steel tubing connected the valve 7 to the gas supply beyond valve 8 and to the pressure gauge J during the addition of gas and the adjustment of the pressure. This valve was fitted with a small blow off plug to permit flushing of the tubing without opening of the valve.

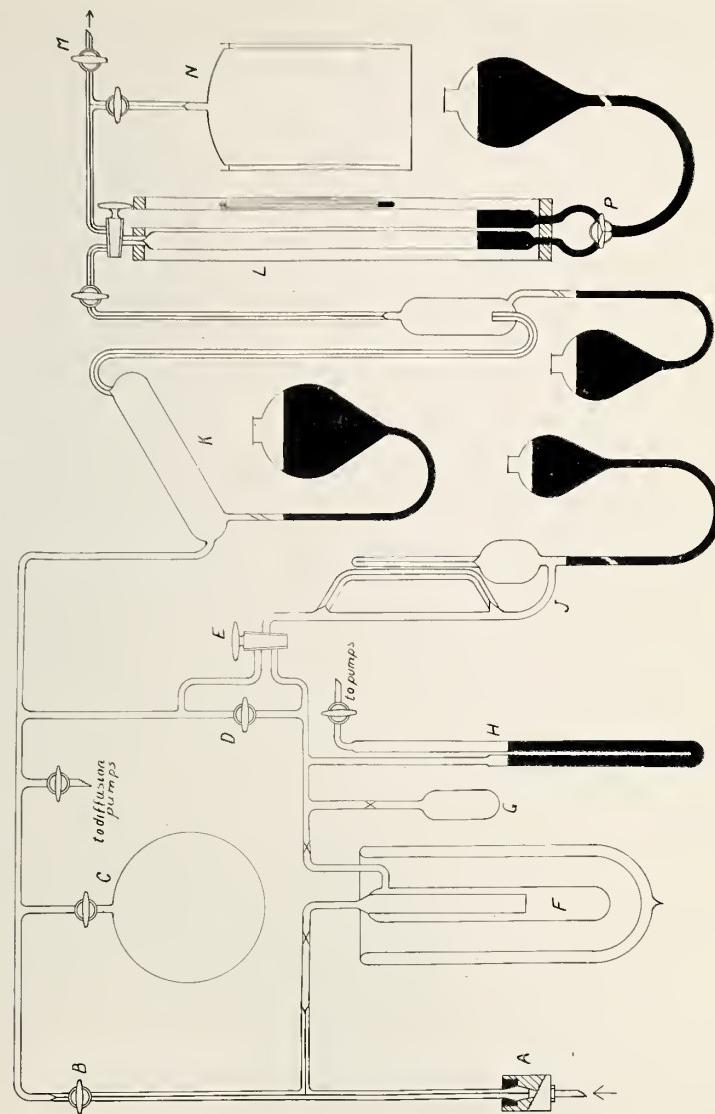
The pipette assembly was pivoted at E and oscillated through about 90° by the crank and connecting rod F. Oscillations were at the rate of 6 per minute. The bath was oil filled and the temperature automatically controlled to 0.03°C. A large U shaped mercury filled thermostat G actuated a sensitive relay which in turn cut in or out a resistance in series with a 400 watt heater in the bottom of the tank. A stirrer, H, carrying two propellers provided efficient circulation of the oil at 600 R. P. M. and, as an aid to temperature control, the metal tank was covered with a layer of insulation. The tank carrying the heater was suspended in such a manner that it could be lowered free of the solubility pipettes when desired.

The purifying system consisted of four stages. Compressed Viking natural gas from storage beyond P was passed over stick sodium hydroxide and anhydrous calcium chloride in the pressure cylinder N, followed by passage over copper metal and copper oxide at 350°C in the small autoclave M, heated electrically by the furnace as shown. A second treatment with sodium hydroxide and calcium chloride followed in L. Lastly the gas passed over activated

charcoal in the pressure vessel K maintained at -20°C . The pressure gauge J was a standard test gauge of 0.5% accuracy. The use of a Bourdon tube gauge in this work was open to criticism and a dead weight piston gauge was obviously preferable. For a preliminary investigation concerned largely with the development of technique, a Bourdon gauge as used was sufficient. Ultimately a piston gauge will be used.

The analysis system shown in Figure 4 was of glass beyond the steel to glass joint A. The material from the pipettes passed by capillary tubing to the condenser F. This condenser was connected to the system by constricted tubing marked X and could be readily sealed off with its liquid condensate. The bulb G was provided for distillation purposes in separating the condensed liquid from the dissolved gas. The stopcock B offered an alternate path to the material from the pipettes and was used after the condenser F was sealed, to remove the last trace of liquid and gas from the pipettes. The one litre bulb G was for the purpose of enlarging the volume of the apparatus during experiments yielding a large amount of gas. Pressures below 1.7 m.m. of mercury were measured on the McLeod gauge J and above this pressure the mercury manometer H was used. The manometer scale was calibrated by a cathetometer correct to 0.004 cm. The condensing section of the apparatus was separated from the pumping section by the stopcock D. The McLeod gauge could be connected to either by means of a two-way stopcock E. A Toepler

FIGURE (4)



pump K was used to transfer the gas at pressures below atmospheric to the measuring burette L. This burette of standard gas analysis form holding 100 c.c. was calibrated with mercury and placed in a water jacket. A parallel tube of the same diameter was connected to the burette and the leveling bulb through the Y stopcock P. Volume readings were made with the two mercury columns at the same height. The burette was calibrated directly to 0.1 c.c. and could be easily read to 0.05 c.c. A temperature reading was given by a calibrated thermometer to 0.1°C immersed in the water jacket and a barometer reading completed the necessary data. The gas from the burette, after measurement, was transferred through the two-way stopcock to the water-sealed glass gas holder N for storage before analysis. Connection to a standard U. S. steel flushing type of gas analysis apparatus was made by capillary tubing and the stopcock M. Analyses were carried out by slow combustion with oxygen over a heated platinum spiral.

The operating procedure during an experiment was as follows. Connection was made from the pumps through the apparatus of Figure 4 to the solubility apparatus. The pipettes were evacuated, all valves excepting 7 being open. Valves 1 and 4 were closed and the copper tube from valve 4 to the union D was disconnected at the union. Purified hexane was allowed to enter through this copper tube by opening valve 4 until sufficient liquid to fill pipette C and half of pipette B had entered. Valve 4 was then closed, and

the copper tube reconnected to the union D. Valve 7 was then connected to the purifying system and the tubing between valves 7 and 8 flushed by opening the blow off plug on valve 7. Gas was admitted to the pipettes at several hundred pounds pressure and blown off a number of times to ensure the removal of air. Finally the pressure was raised to the operating value, valves 7 and 8 closed, the connection at union D with the apparatus of Figure 4 disconnected, and the connection to valve 7 from the purifying system disconnected. The oil bath was raised to position around the pipettes, and oscillation of the apparatus commenced. After one half to one hour at temperature, the oscillation was stopped, connection made from the purifying system to valve 7, and, after flushing the tubing, the pressure in the pipettes was adjusted carefully to the operating value. Valve 7 was then disconnected and the cycle repeated until no discernible pressure drop occurred in the pipettes after one half hour of oscillation. Equilibrium was assumed to be reached and analysis was proceeded with. The pressure drop during the first cycle was approximately 50 lbs. per sq. in. and in four to six cycles became so small as to be beyond the indicating powers of the gauge J. A complete absence of leaks was ensured and maintained by the use of metal to metal joints and a special metallic packing on the valve stems. The behaviour of the high pressure apparatus was excellent in all respects.

When equilibrium was reached, valves 2, 3 and 5, 6 were tightly closed and connection made between the union D and the tube leading

to the analysis system. The whole system, glass parts of Figure 4 and connecting tubing to union D (Figure 3) were evacuated to less than 0.005 m.m. mercury pressure by mercury diffusion pumps backed by a Hyvac oil pump. Stopcocks B and E (Figure 4) were then closed and valve 4 (Figure 3) carefully opened. Referring to Figure 4 condenser F was kept at -20°C and trapped most of the hexane. When the pressure in the apparatus reached atmospheric as shown by the manometer H and the gas burette was approximately full, valve 4 (Figure 3) was closed. The volume and temperature of the gas in the burette were measured at atmospheric pressure and the gas was completely transferred to the holder N. The burette was connected again to the gas supply. This cycle of operations was repeated until the pressure in the solubility pipette was slightly less than atmospheric. The Toepler pump was operated until the hexane in the condenser showed a vapour pressure approximating to that of pure hexane. The condenser was sealed off at the constrictions, allowed to come to room temperature and weighed. The condenser was opened, the hexane removed, and weighed again. After a suitable correction for the weight of air in the empty condenser, the weight of hexane was obtained.

Stopcocks B and E were now opened and evacuation continued with the Toepler pump until the pressure was less than 0.01 m.m. of mercury as shown on the McLeod gauge. At pressures below 2 or 3 m. m. the tedious manual operation of the Toepler pump was

avoided by cutting in an automatic Maass control (not shown), using a water jet pump as a source of power. (55). As sufficient gas accumulated in the receiver of the Toepler pump it was measured in the burette L and transferred to the gas holder N. Usually sufficient hexane accumulated in the latter stages of the process when operating on the liquid phase pipette that liquefaction occurred in the receiver. Sufficient nitrogen was added to take up this liquid hexane as vapour and this gas was stored separately for analysis.

The above process was applied first to the liquid phase pipette. It was desirable to lower the oil bath out of the way in order to make the valves 1 and 4 (Figure 3) easy of access, and it was thought safer to collect the liquid phase first. In collecting the gas phase from pipette A through valve 1 (Figure 3), the same procedure was followed except in one detail. The condenser F was not necessary as no hexane condensed from the gas phase under the conditions prevailing in the apparatus. Consequently no liquid hexane was collected. After emptying the liquid phase pipette and before emptying the gas phase pipette, the whole apparatus was evacuated by diffusion pumps and valve 4 (Figure 3) closed.

The solubility apparatus (Figure 3) was prepared for the next experiment by closing valve 1 and opening valves 2, 3 and valves 5, 6. The volume of the reservoir B was sufficiently great to allow of three or four experiments before adding more hexane.

The gases collected and stored in the gas holder N (Figure 4) were allowed to stand for several hours to ensure uniform composition

before samples were taken for analysis. Not less than four combustions were carried out on each gas collected in the gas holder and average volume taken for the final results. The purified Viking gas used was analysed frequently by combustion in the same apparatus. The calculation of the amounts of hexane and methane in the gas was made in the first place by means of the formulae;

$$(2 \times \text{Volume of CO}_2 \text{ produced} - \text{decrease in volume on burning}) / 7.5 \\ = \text{volume of hexane}$$

$$(\text{Volume of CO}_2 \text{ produced} - 6 \times \text{volume of hexane}) = \text{volume of methane.}$$

Given this volume of methane and knowing the nitrogen content in the original gas used relative to methane, the nitrogen content of the gas from the solubility pipettes may be calculated. Subtracting this from the volume of gas collected leaves the volume of hydrocarbons. The relative amounts of methane and hexane may now be calculated on the basis of the carbon dioxide formed on burning alone. In this manner the use of the decrease in volume on burning is unnecessary and the greatest source of error eliminated. The method is admittedly approximate in that the amount of nitrogen is based on a doubtful value for methane. However the amount of nitrogen is so small that even a 10% error in the first determination of methane will just cause an appreciable error in the nitrogen determination. A 10% error in the first calculation of methane is possible but not probable.

Given the volume of nitrogen by this method the calculation of

the amounts of methane and hexane on the basis of carbon dioxide produced becomes;

$$\text{Volume of hydrocarbons} = \text{volume of gas} - \text{nitrogen content}$$

$$\text{Amount of methane} = (6 \times \text{Volume of hydrocarbons} - \text{carbon dioxide produced}) / 5$$

or,

$$\text{Amount of hexane} = (\text{carbon dioxide produced} - \text{volume of hydrocarbons}) / 5$$

The amount of the second hydrocarbon may be obtained by difference in each case. It will be noticed that the presence of ethane is ignored which is justifiable in that the amount present is less than the error in the method.

Probable error

In a discussion of the errors in this work it can be seen at once that the gas analyses overshadow the other measurements, excepting possibly those on the test gauge. Without doubt the readings on the test gauge were consistent among themselves and reproducible to 2 or 3 lbs. per sq. in., that is to say an error of 0.3% at 1000 lbs. per sq. in. and of 0.1% at 3000 lbs. per sq. in. The absolute values of the pressure were however in doubt, at least to 0.5% and possibly more. In the absence of a dead weight piston gauge, no better accuracy was possible, and for these experiments it is doubtful if greater accuracy was necessary. It was improbable that the test gauge was in error by more than 0.5% considering its careful treatment since purchase. Moreover, as will be seen later, the gas analyses were in error by at least 0.5%.

The volumes of the solubility pipettes were known to better than 0.1% and as a source of error, they may be disregarded.

The measurement of the volume of the gas liberated from the pipettes was a complex process. Reduction to standard conditions and the calculation of the weight of the gas was required. This procedure involved the leveling of two mercury columns, as well as reading the burette, the thermometer, and the barometer. In addition the application of the ideal gas law was assumed. The observations all involved an error of less than 0.1% and assuming that the calibrations were correct, the probable error in the final calculated ^{result} ^ would amount to $\pm 0.3\%$ at the outside. The assumption of the ideal gas law introduced an error very much less than this in the case of methane. Regarding hexane however the error may be appreciable. An equation of state for hexane vapour is not available but for saturated water vapour the error at one atmosphere would be 0.5%. The partial pressure of hexane in the gas was never more than 0.3 atmospheres in the expanded gas and assuming that hexane vapour behaves similarly to water vapour, the error due to the assumption of the ideal gas law becomes less than 0.2%.

The methods of gas analysis used were those commonly applicable to gas mixtures and no great accuracy can be obtained. Readings can be duplicated to 0.2 c.c. in successive combustions, which is an appreciable error when the gas samples are small. With mixtures of methane and hexane the capacity of the apparatus was about 30 c.c.

of gas resulting in a minimum error of about 1%. Furthermore an inspection of the formula given for the gas analyses will show that the amounts of methane and hexane were obtained from the difference between small quantities. Obviously, the error can be much greater than 1% under these circumstances. In order to reduce the error, analyses were repeated at least four times and the mean value taken. The average deviation from the mean value was calculated in each case and is tabled later with the gas analyses. The average deviation varied from 0.4 to 1.1% in the case of methane and from 0.2 to 0.4% for hexane. The deviations in the case of methane may be neglected in comparison with those for hexane since the hexane percentages were never greater than a few percent. The relative probable error in the case of hexane varied from 6 to 12% which is very high. In the case of the liquid phase this error was greatly reduced since the bulk of the hexane was collected as liquid and weighed. However the above error applies to the determination of hexane in the gas phase, the lower limit applying to the highest pressure and the upper limit to the lower pressure. As will be seen later these errors are not sufficiently great to mask the general behaviour of the system investigated. The deviations of the system from that of an ideal solution were enormous, amounting to several hundred percent and increasing very rapidly above 137 atmospheres.

RESULTS AND DISCUSSION

The results of the experiments are tabulated in Tables 7 and 8 and shown graphically, in Figures 5, 6, 7, 8 and 9. For comparative purposes the data for the methane-hexane system at 1 atmosphere has been inserted in Tables 7 and 8. The solubility value is that of McDaniel (46) and the other properties have been taken from the International Critical Tables or calculated on the basis of ideal gases and solutions. The partial molal volume of hexane in the liquid phase was determined graphically from the composition of the liquid phase and its density (56). No equation of state for the phases has been developed although the necessary data is available in Table 7. It is evident that the system does not even approximate to an ideal solution. That the gas phase is far from ideal is shown by the $PV/P_0 V_0$ values as compared to those given for methane (35). The gas phase appears to be very incompressible at the higher pressures and rapidly approaches the liquid state in its properties.

The densities are plotted against pressure for both phases in Figure 5. It is apparent that the maximum pressure used, 205 atmospheres, is not far removed from the critical pressure. Extrapolation as shown gives an approximate value of 236 atmospheres at a density of 0.295 g./c.c.

The data of Table 8 on weight percent of hexane in each phase is shown graphically in Figure 6. It is apparent that the liquid phase obeys Henry's law to pressures somewhat below 130 atmospheres. Above

T A B L E 7

The Properties of the Liquid and Gas Phases at 25°C

Total Pressure	1 atmosphere (1)		69 atmospheres		137 atmospheres		205 atmospheres	
Phase	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas
Volume c.c.	-	-	21.028	11.255	21.028	11.255	21.028	11.255
Weight grams	-	-	13.146	0.6325	12.824	1.353	9.4165	2.5153
Density, grams/c.c.	0.655	0.0013	0.6252	0.0562	0.6103	0.1202	0.4349	0.2235
Volume of expanded gas c.c.	-	-	-	811.4	-	1730.7	-	2709
Partial molal volume of hexane, c.c.	131	-	148	-	106.8	-	105.6	-
Solubility, c.c. methane/g. hexane	0.84	-	105	-	226	-	710	-
PV/P ₀ V ₀	-	1.0	-	0.962	-	1.032	-	1.083
PV/P ₀ V ₀ methane (2)	-	1.0	-	0.990	-	0.918	-	0.902

(1) McDaniel. J. Phys. Chem. 15, 587, 1911.

(2) International Critical Tables. Volume 3; McGraw Hill.

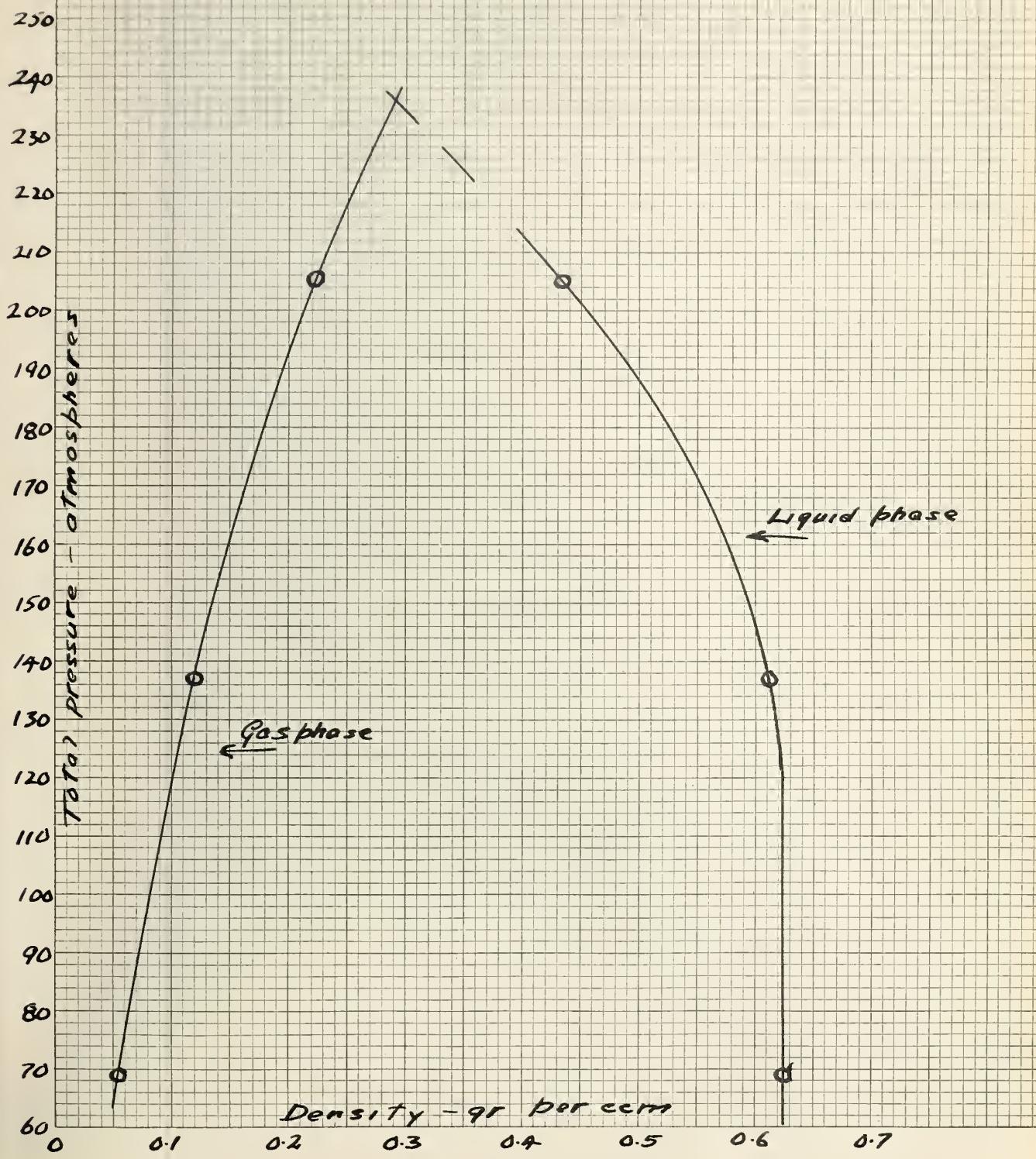
T A B L E 8

The Composition of the Liquid and Gas Phases at 25° C

Total Pressure	1 atmosphere (l)		69 atmospheres		137 atmospheres		205 atmospheres	
Phase	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas
Volume % in expanded gas								
Hexane	-	19.6	-	1.34 ± .2	-	1.49 ± .12	-	6.34 ± .4
Methane	-	80.4	-	94.4 ± .4	-	94.7 ± .5	-	90.7 ± 1.1
Nitrogen	-	-	-	4.3	-	3.8	-	2.9
Weight % in actual phase								
Hexane	1.67	56.7	93.0	6.6	86.1	7.32	64.3	26.2
Methane	98.33	43.3	7.0	86.5	13.9	86.54	35.7	69.8
Nitrogen	0.0	0.0	0.0	6.9	0.0	6.14	0.0	4.0
Mole % in actual phase								
Hexane	0.32	19.6	71.3	1.34	53.5	1.48	24.8	6.34
Methane	99.68	80.4	28.7	94.36	46.5	94.7	75.2	90.7
Nitrogen	0.0	0.0	0.0	4.3	0.0	3.8	0.0	3.0
Calculated partial pressure Hexane atmos.	-	0.196	-	0.97	-	2.29	-	15.2
Methane (diff.)	-	0.804	-	65.15	-	129.51	-	183.8
Nitrogen	-	0.0	-	2.93	-	5.27	-	6.1
Volume % of vapour in expanded gas (ideal)	-	19.6	-	0.203	-	0.0766	-	0.0238
Volume % of vapour in expanded gas (Poynting)	-	19.6	-	0.304	-	0.126	-	0.051

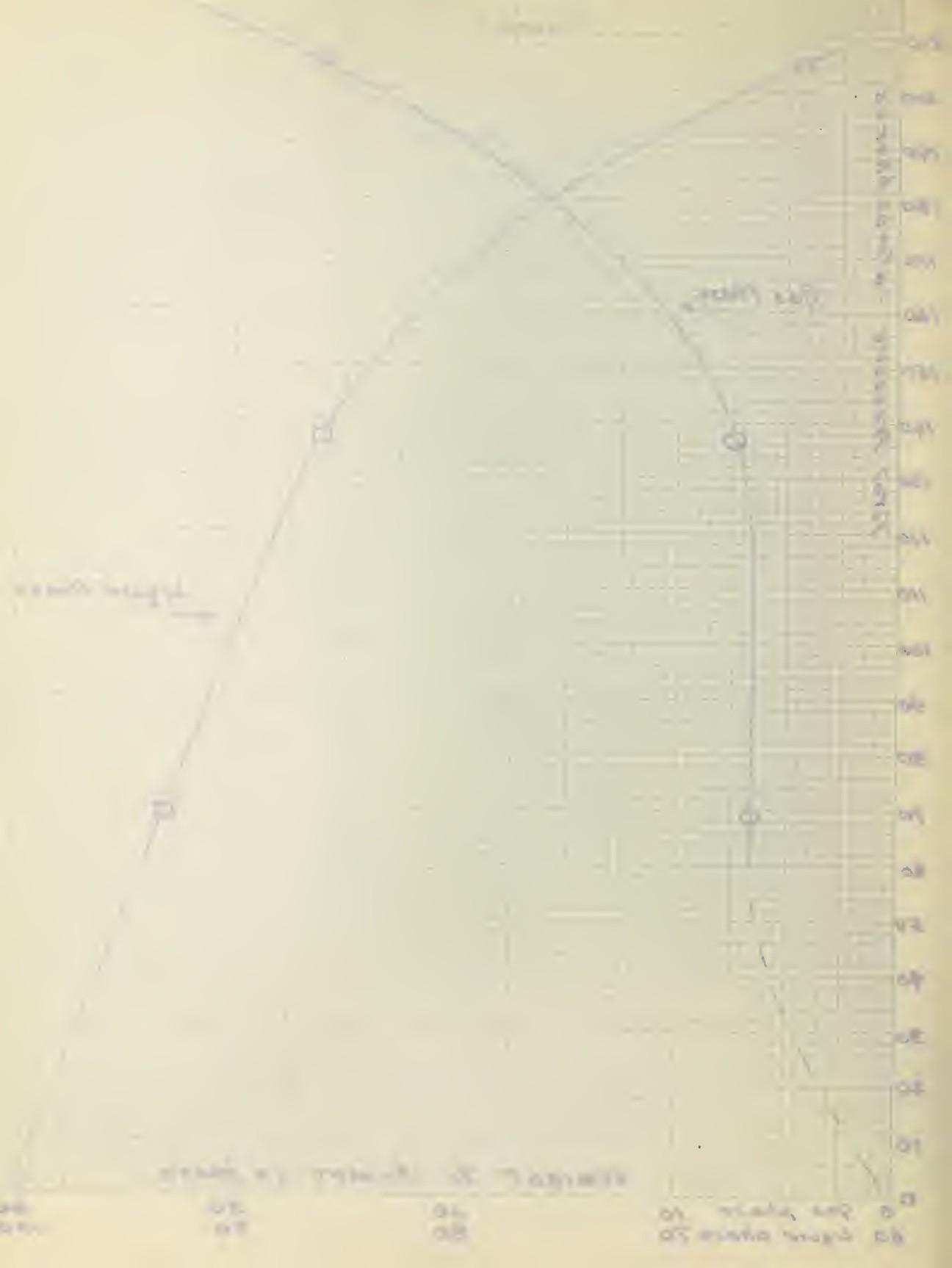
K *M*
L *N*
O *P*
Q *R*
S *T*
U *V*
W *X*
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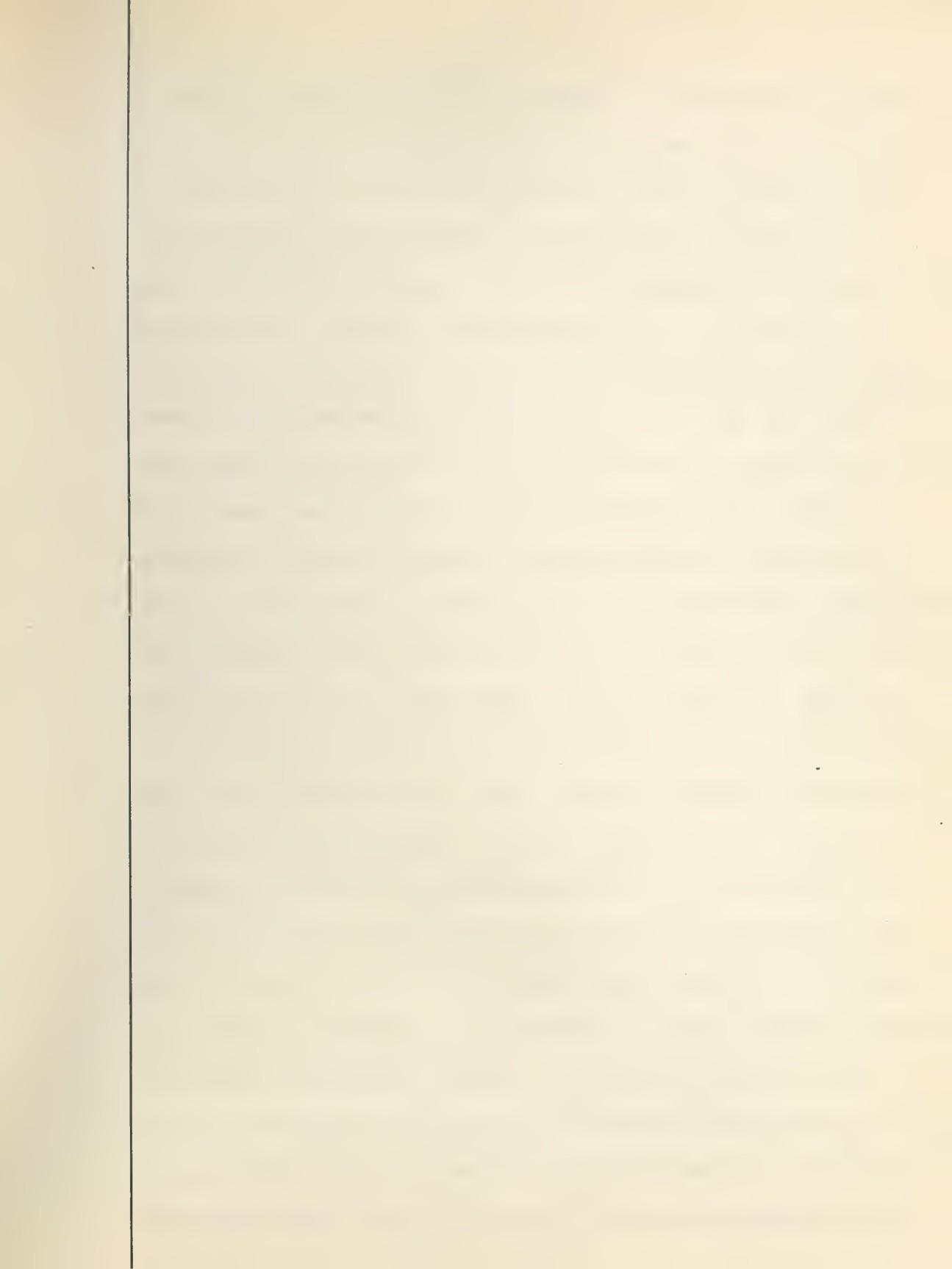
Figure 5



this pressure the deviation is very rapid and shows a decreasing percentage of hexane. It is also apparent that the gas phase does not obey Henry's law at pressures below the lowest used, namely 69 atmospheres. Lacking data, the course of the curve cannot be given but there is undoubtedly an inflection in this range of pressures. At pressures above 130 atmospheres the solubility of hexane in the gas phase increases very rapidly as compared to the slight change in the region 70 to 130 atmospheres. This behaviour is unexpected and may be of the same nature as the observations of Villard (39) that there is a minimum in the solubility of a liquid in a gas. Extrapolation of the curves of Figure 6 gives 238 atmospheres as the critical pressure at a composition of 40% by weight (mole % 14) of hexane in each phase agreeing well with the critical pressure found from Figure 5. It is regrettable that time did not permit measurements at higher pressures so that the course of the curves to the critical point could be plotted with certainty. It is also necessary that measurements be made at smaller pressure intervals over the whole range and at pressures below 69 atmospheres. No empirical equation of state would be of value if based on the available data. These data allow it to be said however, that the solubility of hexane in methane is very large and in fact larger than anything reported by other observers on different liquid-gas systems.

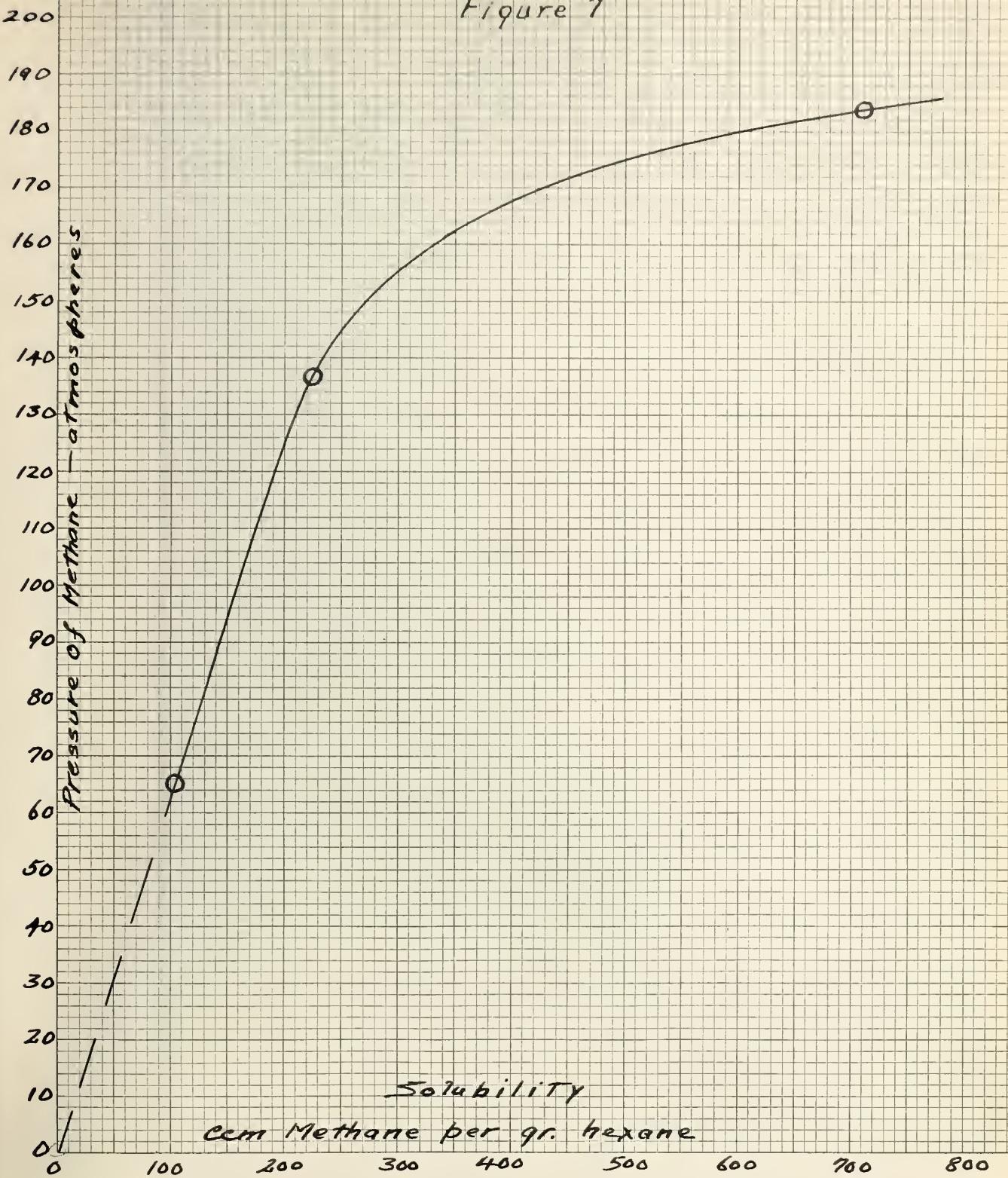
The solubility of methane in hexane is plotted in Figure 7 from the data of Table 7. As was stated before with regard to the liquid phase, Henry's law appears to hold to 130 atmospheres. Above this





pressure, there is a very rapid increase in solubility and it does appear as though the critical point found from other data would be reached. However, lack of intermediate values to those obtained prevents any precise knowledge of the course of the curve. The magnitude of the solubility above 130 atmospheres is of interest in suggesting one source of gas liberated with the petroleum from an oil well. In technical units, the gas in solution at 200 atmospheres amounts to approximately 2000 ft. per barrel. This is a higher ratio than usual in oil wells but oil well pressures are usually less than 200 atmospheres. The gas in solution does not however begin to account for the gas liberated, carrying naptha, in areas such as the Turner Valley field. The gas phase in these experiments approximates more closely to the combined product of that field. This is also the case in the work of Lindsly (53), already referred to. The gas-oil ratio in the gas phase at 100 to 130 atmospheres is in the neighborhood of 20,000 cu. ft. per barrel, which is the ratio for the best wells in the Turner Valley. It would suggest that there is no movement of liquid in the producing zone of the Turner Valley but that the product there is the gas in solution in the liquid phase. That the gas-oil ratio in the Turner Valley averages about 150,000 and reaches 1,000,000 cu. ft. per barrel in some cases would suggest that there is no liquid reservoir. It should be borne in mind however that there is little relation between the operations in the Turner Valley and controlled laboratory experiments on a single two component system at 25°C. The gas-oil ratio at a producing well

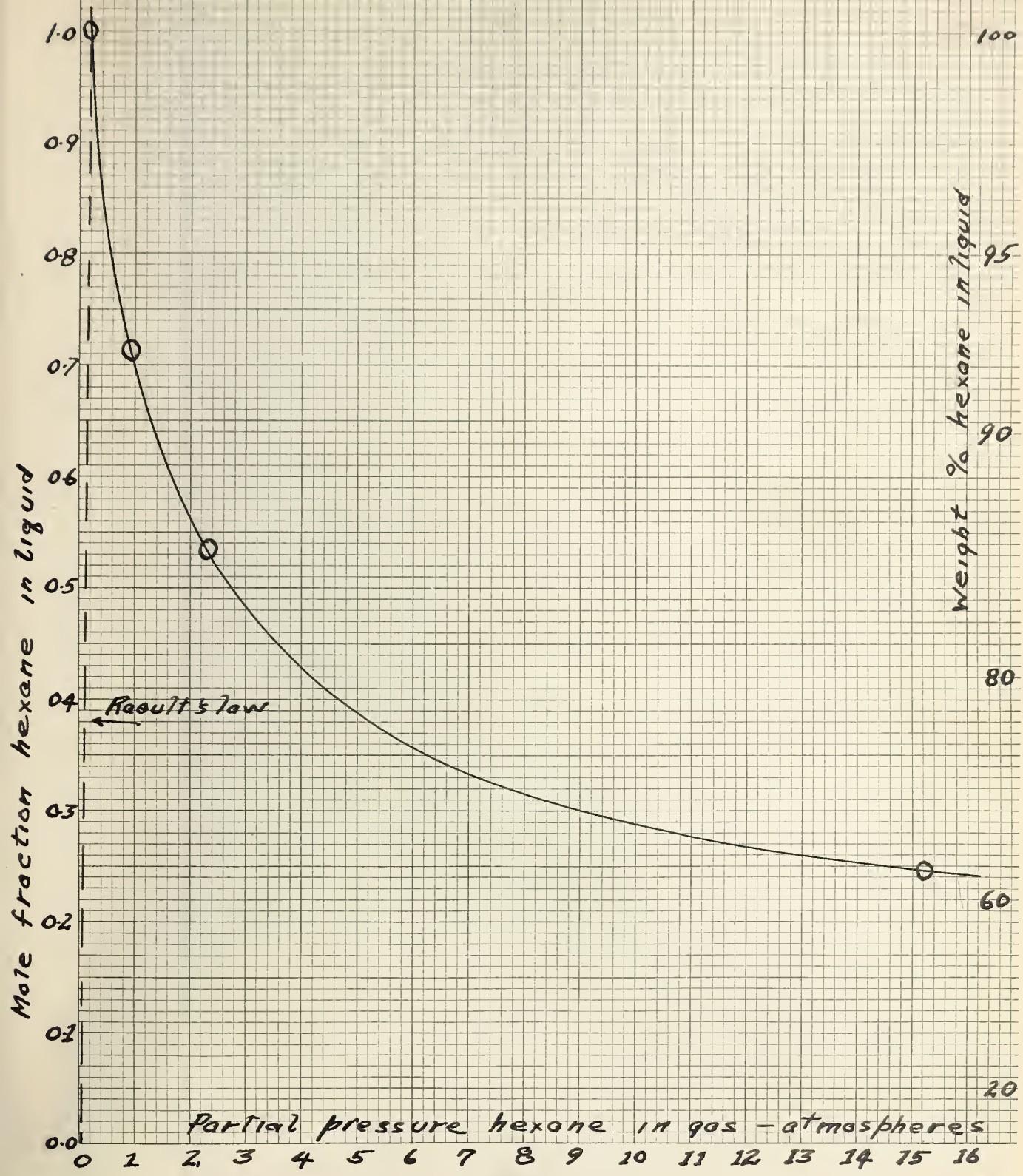
Figure 7



varies greatly with the operating procedure and the state of the hole. Moreover, the temperatures at the bottom of a well are certainly much higher than 25°C and any exact comparison is not at present possible. One conclusion can be drawn however without being subject to doubt on consideration of Figure 6. The higher the operating pressure the greater will be the concentration of vapours in the gas removed from the well.

The partial pressures of the constituents in the gas phase are given in Table 8 and plotted in Figure 8 against mole fraction (mole % / 100) and weight percent of hexane in the liquid phase. The partial pressures are only approximate in that they were calculated on the assumption of the ideal gas law with the aid of the measured concentrations. The error with nitrogen is small but to assume the ideal gas law for hexane vapour above 1 atmosphere introduces a serious error. No other procedure was possible however without more data. The partial pressure of methane was found by difference. It is at once evident that the partial pressure of hexane reaches enormous values, of quite a different order from the partial pressure of water in compressed nitrogen over water, (44), for instance. The effect of the solubility of a liquid in a gas is shown in Figure 8 in a more pronounced manner than in any of the previous graphs discussed and shows, moreover, that the effect is enormously greater than any of the experimental errors previously discussed. The result of Raoult's law assuming the solution to be ideal is shown by the broken line and it is at once evident that Raoult's law only applies

Figure 8



in extremely dilute solution. The similarity in properties of methane and hexane would lead to an expectation of better agreement. In fact the excellent agreement with Raoult's law shown by solutions of two liquids of like chemical properties (36), would suggest that the deviation is not due to a failure in Raoult's law but is an effect due to the pressure as already emphasized. The change in the vapour pressure of hexane with pressure is in the opposite direction to that predicted by Raoult's law and of such magnitude to make it very probable that there is no connection with Raoult's law.

The volume % of hexane in the expanded gas phase as given in Table 8 is plotted in Figure 9 against the total pressure. The calculated % of hexane given by the ideal equation (1) above, are also given in Table 8 and plotted on Figure 9. Obviously there is no agreement. Of more interest are the results of Poynting's rule. The values of the % hexane in the expanded gas were calculated from equation 4 above. The partial molal volumes are given in Table 7, the vapour pressure p_0^1 was calculated on the assumption of Raoult's law from the composition of the solutions as given in Table 8. The coefficient of compressibility used was taken from the International Critical Table and was an average value for pure hexane over the range 100 to 300 atmospheres. The value was 117×10^{-6} . Inspection of the data given in Table 8 and of the curve on Figure 9 shows that there is no agreement between the observed results and the results of Poynting's rule applied as above.



The increase in vapour pressure of hexane as observed is of a quite different order from the increase predicted by Poynting's rule. The fault cannot lie with Poynting's rule as it is a direct consequence of the laws of thermodynamics but rather with the manner of application. The compressibility of pure hexane cannot be even approximately equal to the partial compressibility of hexane in the solutions investigated. Moreover, the application of the ratio $PV/P_0 V_0$ to methane mixed with the relatively large amounts of hexane found is not admissible. Before Poynting's rule can be applied to systems such as that investigated, a determination of compressibilities on the liquid phase at various concentrations is necessary and equally important, the equation of state and the partial molal quantities of the constituents of both phases must be found. All the data necessary except that required for compressibility appears in Tables 7 and 8 but the accuracy is not sufficient nor are the number of determinations and the range of pressures large enough to warrant the calculations necessary. Lastly, experiments over a range of temperatures are necessary for a complete discussion of the system.

In conclusion it is desirable to point out that an adjustment in the conceptions of the relations of a gas to a liquid may be justified. In general it has been assumed that the solubility of a liquid in a gas was small and of minor importance except at very high pressures. It would appear however that with certain systems the solubility may be relatively great and of the same order as the

solubility of the gas in the liquid at moderate pressures. The critical pressure indicated for the present system of 236 atmospheres is only a fraction of that to be expected from a consideration of the widely separated critical temperatures of the components. It can only be assumed, that a gas of similar chemical properties to the liquid, can dissolve that liquid readily as soon as the molecular concentrations become at all comparable. As the liquid dissolves in the gas, the properties of the two phases approach one another and further solution is caused so that with increasing pressure the solubility increases at a rate greater than proportional to the pressure. Evidently, complete miscibility of the two components, even if of widely separated critical temperatures, so long as they are similar chemically, will occur at a pressure that is not excessively high.

SUMMARY

An apparatus has been described that is capable of the investigation of two phase liquid-gas systems at pressures to several hundred atmospheres over a range of temperature.

Preliminary experiments on a simple two component system, methane and hexane, have been carried out and proved the satisfactory performance of the apparatus.

The composition and physical properties of the two phases have been determined approximately at 25° C; at 69 atmospheres pressure; 137 atmospheres pressure and 205 atmospheres pressure.

It has been shown that Raoult's law and Henry's law fail completely at relatively low pressures and that at 205 atmospheres the deviations are enormous. The solubility of the liquid component hexane in the gaseous component methane increases very rapidly with pressure, the two probably being completely miscible above 240 atmospheres.

The results have been discussed in relation to oil well operation and in relation to the theory of such systems.

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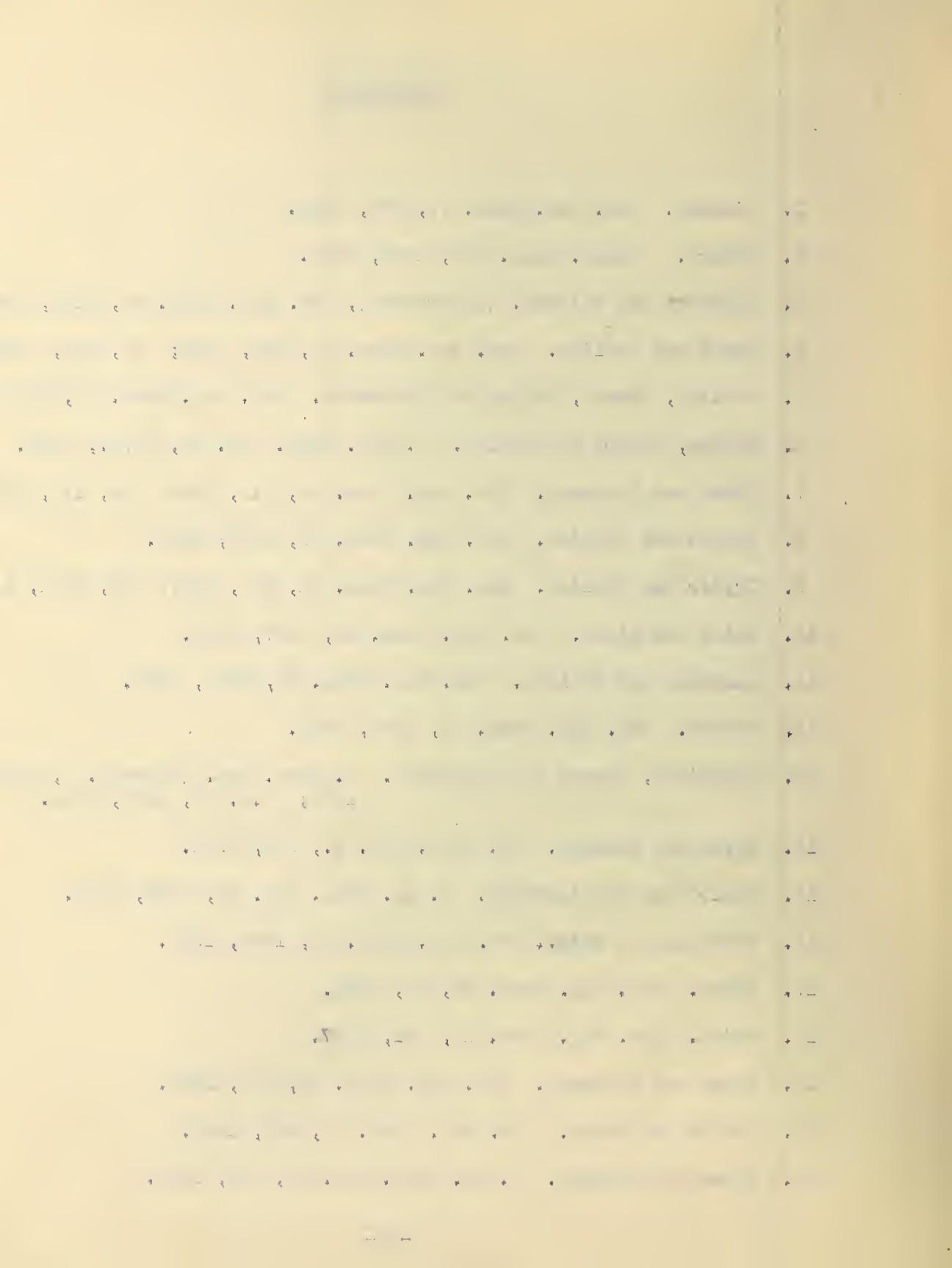
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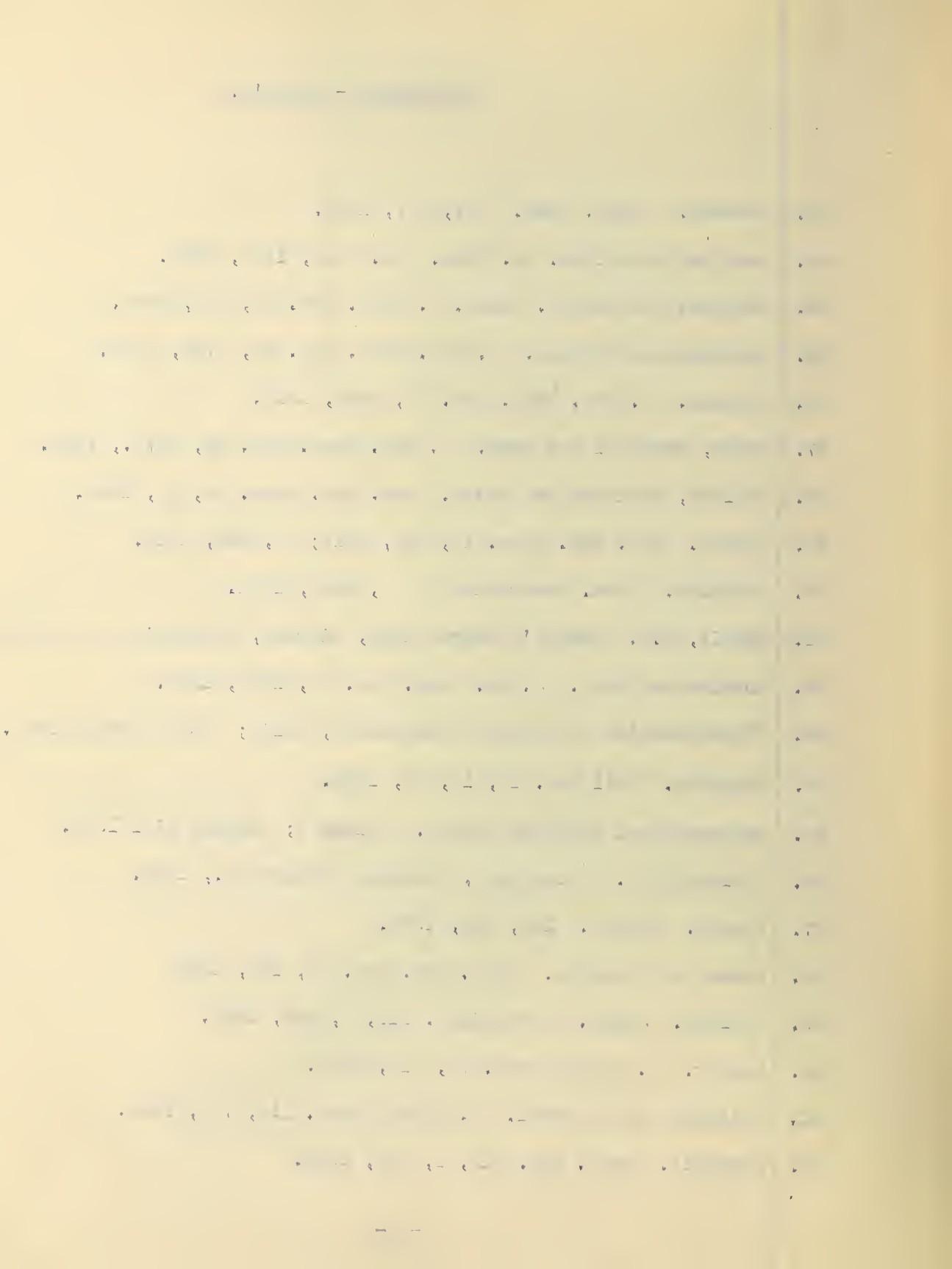
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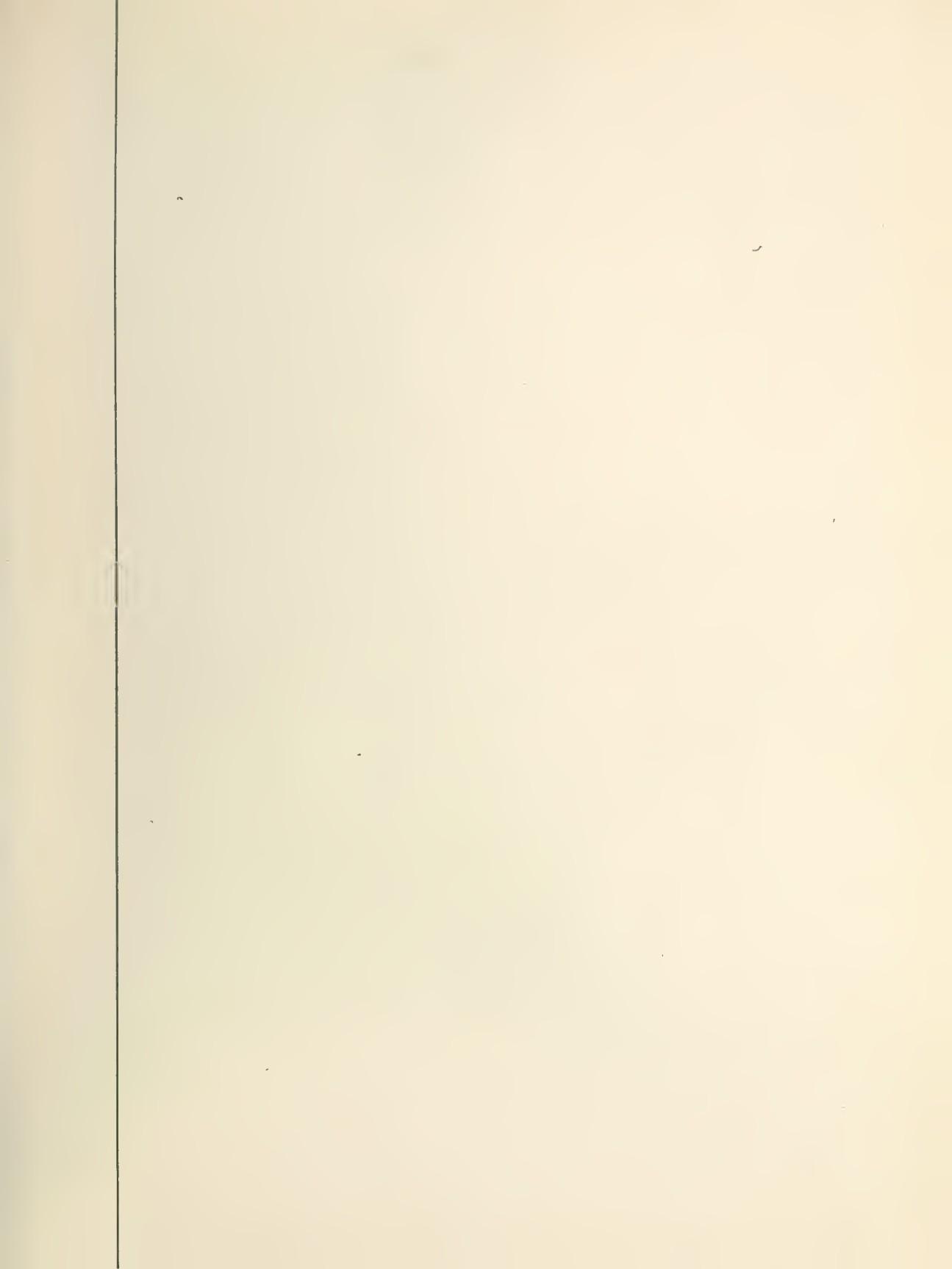
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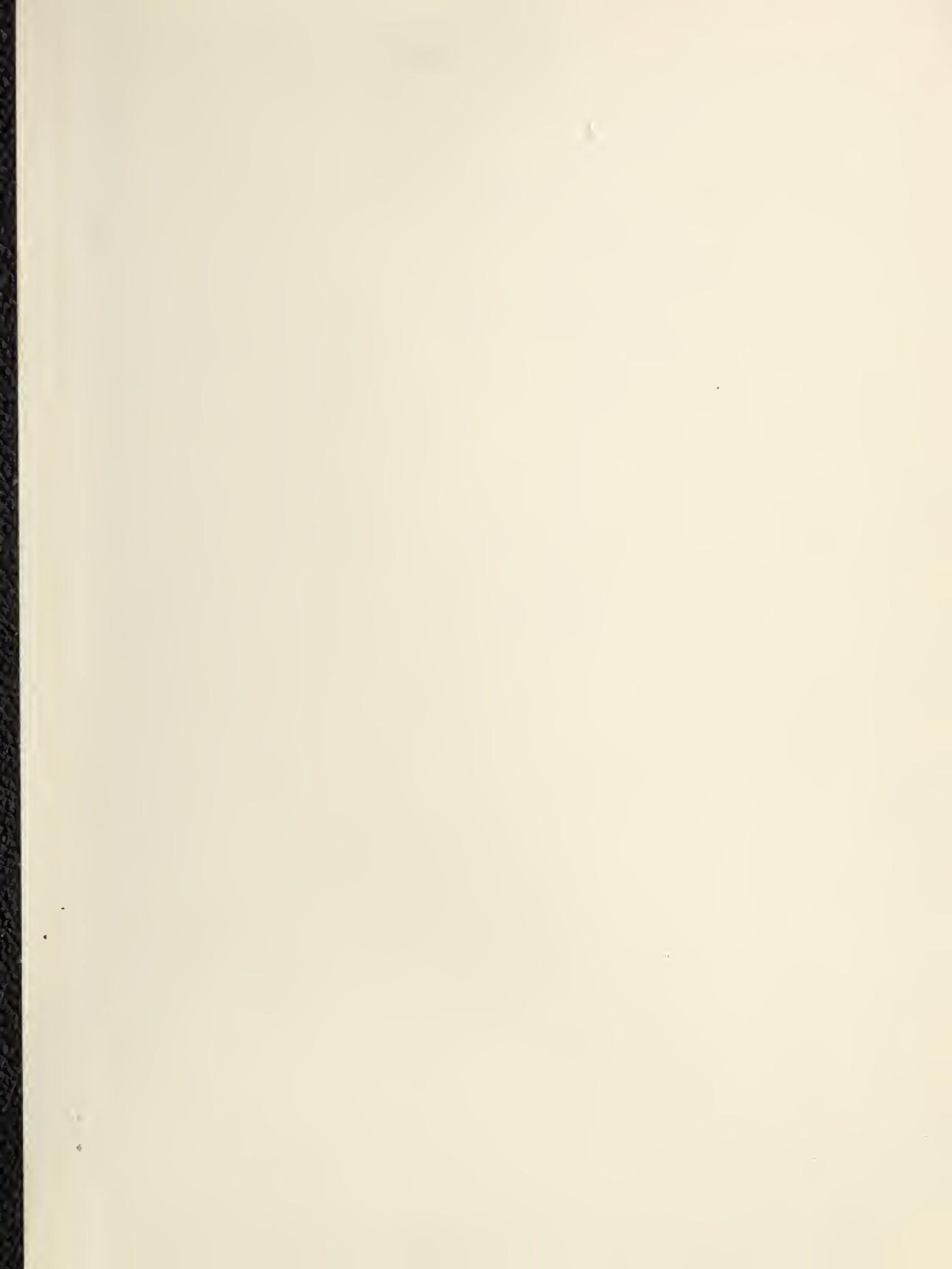
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